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SECTION-A

PART IV

Determination of carbosulfan and propoxur in environmental samples employing p-amino-acetanilide

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Abstract

A simple, rapid, sensitive and accurate spectrophotometric method is developed for the determination of carbosulfan and propoxur in field water samples and grains. The method is based on the formation of coloured species upon coupling their hydrolysis products with diazotized p-aminoacetanilide, exhibiting maximum absorption at 390 and 389 nm respectively. The method obeys Beer's law over the concentration range 0.5 - 12 and 0.5 - 16 µg/ml.

(**Keywords.** spectrophotometry/carbosulfan, propoxur determination / p-amino-acetanilide / chloroform)

Introduction

Carbosulfan, carbamic acid [(dibutylamino)thio]methyl-2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester is a recently developed broad spectrum systemic and contact insecticide belongs to the class of carbamate insecticides. It is used for the control of soil dwelling insects and foliar pests on maize, potatoes and sugarbeet and also used as a nematicide. It acts as a cholinesterase inhibitor. Carbosulfan is unstable in acid

medium and it will be converted into carbofuran by N-S bond cleavage. Clay *et al*¹, have reported the activity of this compound

Propoxur, 2-(1-methyl ethoxy) phenyl methyl carbamate also belongs to carbamate class of pesticides. It is a white crystalline solid having m.p. 91°C, soluble in most organic solvents. Propoxur is commercially available as 1% Baygon spray, 2% bait, 4% Baygon and 70% wettable powder. Baygon has rapid knockdown and long residual action. It shows cholinesterase inhibiting properties and is particularly effective as an insecticide. It is particularly effective against insects affecting man and animals, such as cockroaches, flies and mosquitoes. Foilage sprays have given effective control of aphids, lygus bugs, grass hoppers and other insects on various crops. Bioactivity and persistence of propoxur in mineral soil, river water and in the aquatic environment have been reported²⁻⁴. Wide spread application of these carbamate pesticides to control pests in agricultural as well as domestic applications. All these pesticides from the agricultural field, and domestic applications are washed over the nearby water sources either by leaching or by the surface runoff. Such residue concentration are more than the permissible levels and are generally harmful to pond fauna and the people who drink these waters.

Literature survey revealed that very few analytical methods such as GC⁵⁻⁶, HPLC⁷⁻¹¹ and TLC¹²⁻¹⁵ and some other spectrophotometric methods¹⁶⁻²³ have already been reported. The present communication reports a new spectrophotometric method for the determination of the above pesticides based on the formation of a coloured species by coupling the corresponding phenols obtained by alkaline hydrolysis with diazotized p-aminocetanilide.

Materials and Method

All chemicals used were of analytical grade and all of the solutions were freshly prepared with distilled water. A Hitachi, model U-3400, UV-VIS NIR Spectrophotometer with 1 cm glass cells was used for absorbance measurement. Sodiumhydroxide (2%) and sodiumnitrite (0.5%) solutions were freshly prepared. p-aminoacetanilide solution (0.1%) is prepared in 100ml 1N hydrochloric acid.

Preparation of standard solutions of Carbosulfan and Propoxur (50 µg/ml) :

Stock solution of the above pesticides were prepared by dissolving 50 mg of analytical grade insecticide in 100ml of methanol. From this working standard solution is prepared by diluting 10 ml of this solution to 100ml.

Preparation of sample solution .

Formulations: Carbosulfan 25% and Propoxur 70% wettable powder. An amount equivalent to 50 mg of the insecticide was dissolved in 50 ml of methanol. 5 ml aliquots of the solution was subsequently diluted with 100ml of methanol.

General Procedure :

Aliquots of standard insecticide solution (50µg/ml) 0, 0.25, 0.5, 1.0,, 6ml were placed in series of 25 ml standard flasks followed by adding 2.5ml of 2% sodiumhydroxide and 2.4ml of diazotization mixture. The solutions were made to the mark with distilled water and absorbance was measured for the yellow coloured chromophore against a reagent blank. The absorbance is plotted against the final concentration to obtain a calibration graph.

Water samples : pH of each water sample was adjusted to 3-4 with 20% sulphuric acid. One litre samples of distilled water and tap water was fortified with different concentrations of insecticide dissolved in methanol. The fortified water samples were extracted with 100ml chloroform using a separating funnel. Chloroform extracts were collected into a funnel and re-extracted the aqueous phase twice with 50ml chloroform. The combined extracts were washed with 0.1 M potassium carbonate solution and dried over anhydrous sodium sulphate in a filter funnel and collected the extracts in a 250ml standard flask. Finally these were made upto the mark with chloroform. Known aliquots of the chloroform were evaporated to dryness on a steam bath. The residue was dissolved in methanol, then developed the colour.

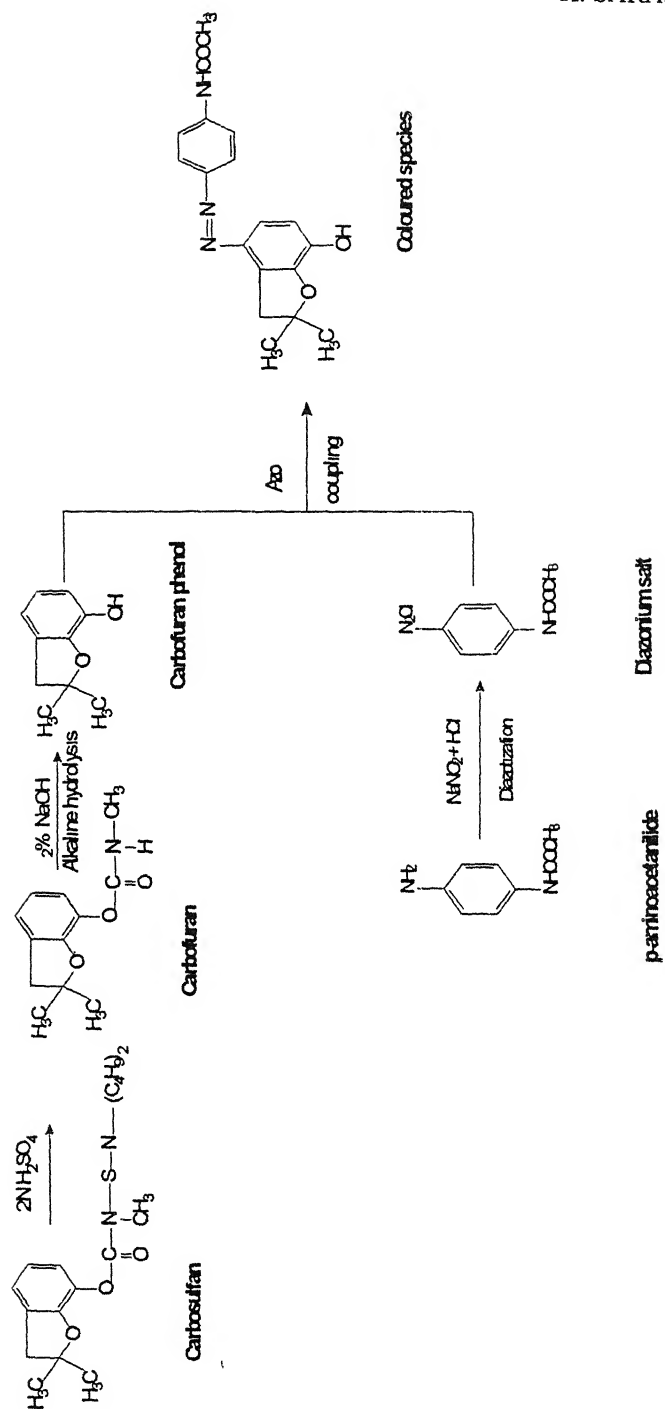
Grains : 100g of grains (rice and wheat) was taken in a conical flask and shaken for 5 min, with 200ml chloroform. Chloroform was filtered into a 250ml standard flask through a Whatman No.1 filter paper and residue was washed twice with 10ml chloroform. Chloroform extracts were combined and made up to the mark. Known aliquots of the chloroform extracts were used for colour development after evaporating chloroform.

Results and Discussion

The absorbance maximum was at 390nm for Carbosulfan and 389nm for Propoxur. Beer's law is obeyed over the range 0.5-12 µg/ml for Carbosulfan and 0.5-16 µg/ml for Propoxur. The colour develops instantaneously and remains stable for more than 24 h. The coupling reaction can be done at room temperature only.

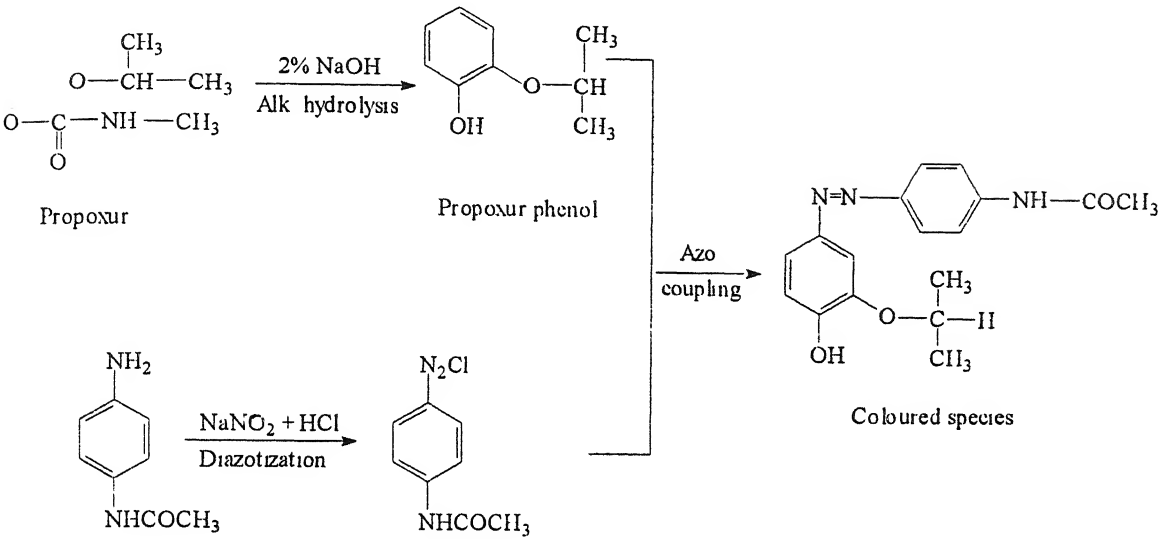
The suitability of the proposed method was studied by analysis of ten replicate samples containing 5ppm of Carbosulfan and Propoxur. The relative error and relative standard deviations are given in Table 1.

Reaction Mechanism



Carbosulfan with p-aminoacetanilide

Reaction Mechanism



p-aminoacetanilide

Propoxur with p-aminoacetanilide

Table 1– Characteristics of the method

Parameter	Carbosulfan		Propoxur	
	Present work	Reference method ¹⁹	Present work	Reference method ¹⁸
λ_{max} , nm	390	475	389	500
Beer's law limit, $\mu\text{g/ml}$	0.5-12	1-10	0.5-16	0.25-5.0
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.0083	-	0.0125	-
Molar absorptivity, $\text{litre mole}^{-1} \text{cm}^{-1}$	4.576×10^4	-	1.674×10^4	-
Stability of the coloured species, hr	24	8	24	12
Relative Standard Deviation, %	0.91	0.8	0.4	0.6
Relative Error, %	0.5	0.6	0.2	0.3

Formulations containing Carbosulfan and Propoxur were analysed (10 replicates). For a 25% Carbosulfan emulsion the mean \pm standard deviation was $24.48 \pm 0.12\%$. For a 1% Propoxur spray and 4% dust the corresponding values were $0.96 \pm 0.08\%$ and $3.84 \pm 0.02\%$ respectively.

Recovery experiments were performed with known amounts of the compounds added to different samples of grains and water. For water samples a methanol solution of the insecticides was added. Grain samples were spiked by adding a methanol solution of the insecticide to the dry grains and evaporating the solvent.

The results presented in Table 2 show that recovery was in the range 95 to 97%. The results in Table 3 suggest that the method is applicable to the analysis of field water samples also.

Table 2— Recovery of Carbosulfan and Propoxur from grains and spiked water samples.

Sample	Carbosulfan			Propoxur		
	Recovery, %			Recovery, %		
	Added, ppm	Present work	Reference method ¹⁹	Added, ppm	Present work	Reference method ¹⁸
Rice	1.0	$96.4 \pm 1.9\%$	96.0 ± 1.6	1.0	96.5 ± 1.6	96.0 ± 1.2
	3.0	$96.2 \pm 1.0\%$	96.0 ± 1.2	3.0	96.25 ± 1.0	96.0 ± 1.0
	5.0	$95.4 \pm 0.9\%$	94.8 ± 0.8	5.0	96.17 ± 0.8	95.8 ± 0.8
	7.0	$94.8 \pm 0.7\%$	93.5 ± 0.6	7.0	95.38 ± 0.6	94.7 ± 0.6
Wheat	1.0	$96.40 \pm 1.2\%$	95.0 ± 1.4	1.0	97.0 ± 1.4	96.0 ± 1.4
	3.0	$96.20 \pm 1.0\%$	94.1 ± 1.0	3.0	96.50 ± 0.9	95.6 ± 1.0
	5.0	$95.17 \pm 0.8\%$	93.2 ± 0.7	5.0	96.33 ± 0.5	94.7 ± 0.9
	7.0	$95.00 \pm 0.6\%$	92.8 ± 0.5	7.0	95.63 ± 0.4	93.0 ± 0.7
Water	1.0	$96.20 \pm 1.0\%$	96.0 ± 1.6	1.0	97.5 ± 1.2	97.2 ± 1.0
	3.0	$96.75 \pm 1.0\%$	96.0 ± 1.2	3.0	97.75 ± 0.9	97.0 ± 1.0
	5.0	$96.0 \pm 0.9\%$	95.2 ± 0.8	5.0	96.5 ± 0.7	96.3 ± 0.9
	7.0	$95.60 \pm 0.7\%$	94.6 ± 0.7	7.0	95.5 ± 0.6	95.1 ± 0.7

Table 3— Determination of Carbosulfan and Propoxur in field water samples

Sample Volume, ml	Carbosulfan found, ppm		Propoxur found, ppm	
	Present work	Reference method ¹⁹	Present work	Reference method ¹⁸
250	0.20	0.20	0.18	0.14
250	0.30	0.29	0.28	0.26

The results obtained by the proposed method are found to be superior to the reference methods¹⁸⁻¹⁹. The method can be compared favourably with the reported methods¹⁸⁻¹⁹. As of its favourable characteristics as regards its stability, sensitivity and selectivity, the method can find applications to the field water samples also.

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Synthesis and characterization of Mn(III), Fe(III), Zr(IV), Th(IV), VO(II) and UO₂(II) chelates with 4,4'-dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine

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Abstract

4,4'-Dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine (DDPBPD) and its chelates with Mn (III), Fe (III), Zr (IV), Th (IV), VO(II) and UO₂(II) have been synthesised. These chelates have been characterized on the basis of elemental analysis, magnetic susceptibility, IR, electronic spectra and TGA analysis. The I.R. spectral studies indicate that the ligand acts as a dibasic tetradentate and coordinates through phenolic OH and azomethine nitrogen. The dependence of the electrical conductivity on the temperature has been studied over the temperature range 300-520 K and the chelates are found to show semiconducting behaviour. Thermogravimetric studies indicate the presence of water molecules in the Fe (III), Zr (IV) and Th (IV) chelates.

(**Keywords** IR/electronic spectra/polyschiff base/polychelates/TGA/electrical conductivity)

Introduction

Polymeric co-ordinating reagents are a novel type of substance possessing a combine action of the physical properties of high polymer and the chemical properties of the attached reagents¹. The facile regenerability, higher stability and operational flexibility of the co-ordination polymers have created considerable research interest in the recent years². The present paper describes the synthesis and characterization of chelates derived from 4,4'-dihydroxy-3,3'-dipropylbiphenyl-*o*-phenylenediamine. (DDPBPD).

Materials and Method

All the chemicals used were of Analar grade. DMF, ethanol and methanol were used after distillation. 4,4'-Dihydroxy-3,3'-dipropylbiphenyl (DDPB) was prepared by

Friedel-Crafts reaction. Manganese(III) acetate dehydrate was prepared³ by the oxidation of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$.

Preparation of ligand

The ligand DDPBPD was prepared by refluxing a mixture of DDPB and *o*-phenylenediamine in 1:1 molar ratio in dry ethanol for 3 h. The resulting pale yellow solid was filtered and washed several times with hot water followed by ethanol and air dried. The product was insoluble in water and common organic solvents but soluble in hot DMF. The product was crystallised from hot DMF. The purity of the ligand was checked by tlc. Yield (5.0 g, 68 %), m p 322 °C.

Synthesis of polychelates

A solution of DDPBPD (0.01 mol) was prepared in DMF (25 ml), a suspension of the metal salts [$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, ferric chloride, vanadyl sulphate, zirconyl chloride and nitrates of Th and UO_2] in DMF-EtOH (1 : 4 v/v) (0.01 mol, in 25 ml) were added dropwise with constant stirring. A saturated solution of ammonium acetate was also then added with rapid stirring. On refluxing the mixture on a water bath for 6-7 hours, solid were separated out, washed with hot water, DMF, EtOH and acetone and dried over fused CaCl_2 .

Carbon, hydrogen and nitrogen analyses of the ligand and polychelates were carried out on a Carlo Erba 1108 at microanalytical section Central Drug Research Institute, Lucknow. The metal content of the polychelates were determined volumetrically and gravimetrically⁴ (using a mixture of concentrated hydrochloric, nitric, per chloric and sulphuric acids) IR spectra in KBr pellets were recorded on a Perkin-Elmer 842 IR spectrophotometer. Electronic spectra were recorded on a PAS-2 spectrophotometer at BARC Mumbai. The magnetic susceptibility measurements were carried out at room temperature by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. The diamagnetic correction were taken from a standard source. Thermogravimetric analysis was performed on a Perkin-Elmer TGS-2 thermobalance with heating rate $10^\circ \text{ min}^{-1}$ in air atmosphere at RSIC, Nagpur. For the electrical conductivity measurements a pellet of the polymer under study was prepared by pressing a finely powdered and dried sample under hydrostatic pressure at 20,000 lb in^{-2} for two min. A uniform thin layer of silver paste was applied to both sides of the pellet, providing electrical contacts. The average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed through the pellet holder for connections. The entire assembly was placed in furnace. It was

heated at a rate of $1\text{ }^{\circ}\text{C min}^{-1}$. The resistance of the pellet was measured by Zentech 702 A high resistance meter.

Results and Discussion

All the polychelates are coloured amorphous solids, insoluble in water and common organic solvents. The analysis of the compounds agrees with expected 1:1 (metal: ligand) composition. The solids do not melt sharply but with decomposition. All the chelates are stable in air for extended periods of time.

In the IR spectra of ligand medium broad band at 3237 cm^{-1} due to intramolecularly hydrogen bonded OH stretch, disappeared in the spectra of all polychelates indicating that the deprotonation of OH and its involvement in coordination⁵. The shift of C-O from 1240 to 1280 cm^{-1} supports bonding of ligand through the phenolic oxygen. The ligand band at 1638 cm^{-1} due to central C=N stretch, shifted to lower frequency 1590 cm^{-1} on chelation confirming the coordination through azomethine nitrogen atom to the metal ions. The bands at 970 and 900 cm^{-1} in the spectra of VO(II) and UO₂(II) polychelates were attributed to V=O and O=U=O stretches respectively. New bands observed in the region $450\text{--}650\text{ cm}^{-1}$ are assigned to M-N and M-O modes of vibration respectively⁶.

The Zr(IV), Th(IV) and UO₂(II) polychelates are found to be diamagnetic as expected. The electronic spectra of UO₂(II) polychelate exhibits charge transfer bands in the regions $32500\text{--}33200$ and $35300\text{--}36100\text{ cm}^{-1}$ assigned to $n \rightarrow \pi$ and $\pi \rightarrow \pi$ transitions respectively^{7,8}. Low intensity band appearing around at 20000 cm^{-1} shows the presence of symmetrical O=U=O stretching frequency⁹. The VO(II) polychelate has magnetic moment 1.79 B.M. and exhibits bands at 11764 , 17182 and 25974 cm^{-1} due to $d_{xy} \rightarrow d_{xz}$, d_{yz} , $d_{xy} \rightarrow dx^2-y^2$ and $d_{xy} \rightarrow dz^2$ transitions, respectively, towards square pyramidal stereochemistry⁵. The Fe(III) polychelate shows a magnetic moment value 5.97 B.M. correspondence to five unpaired electrons. The electronic spectra of this polychelate exhibits bands at 23255 , 18939 and 17791 cm^{-1} , which are assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_{1g}$, respectively¹⁰. From the electronic spectra and magnetic studies it is evident that Fe(III) polychelate possesses high spin octahedral configuration. The electronic spectrum of Zr (IV) polychelate exhibits single intense charge transfer band in the region $24860\text{--}28360\text{ cm}^{-1}$ which is consistent with $(n-1) d^0 ns^0$ electronic configuration. The Mn(III) polychelate shows magnetic moment value 4.95 B.M. expected for a high spin complex with four unpaired electrons. The electronic spectra of Mn(III) polychelate exhibits intense and sharp band around at 22700 cm^{-1} and

another set of band in the region 12000-18520 cm^{-1} are observed. The band around at 22500 cm^{-1} is assigned to a charge transfer because of its high intensity. This assignment is in agreement with those of previous workers^{11,12}. The splitting of $d-d$ transition band in to a number of bands in the region 12000-18520 cm^{-1} may be explained on the basis of a strong Jahn-Teller effect expected for a d^4 ion and lowering of symmetry from octahedral.

The thermograms of these polychelates show two steps decomposition. The initial weight loss is due to the loss of two coordinated water-molecules present in the case of Fe (III), Zr (IV) and Th (IV) chelates. On further heating organic component of the chelates decompose leading to formation of metal oxide¹³. The activation energy was calculated from the Broido¹⁴ plots of $\ln (\ln 1/y)$ vs $T^{-1} \times 10^3$. Since the plots are straight lines, the rate of the reaction is believed to be one over the entire range of decomposition. The higher value of activation energy suggests the higher stability.

The d. c. electrical conductivity of ligand and its polychelates was measured in their pellet form in the temperature range 300 - 520 K. (Table 1). The electrical conductivity varies exponentially with absolute temperature according to relation $\sigma = \sigma_0 \exp (-Ea/kT)$, where σ_0 is a constant, Ea is activation energy and k is the Boltzmann constant.

In all the cases electrical conductivity increases with increasing temperature indicating these chelates lie in the range of typical semiconductor¹⁵. It was observed that, there are two distinct regions. In the low temperature region the slope of plots have small values and extrinsic conduction may present in the chelates. In the high temperature region, a linear dependence of $\log \sigma = F (1/T)$ was observed. In this temperature domain the chelates may behave as intrinsic conduction. The lower temperature range is the region of extrinsic semiconductors where the conduction of carriers from linear localized band to the conduction band. At the higher temperature range, the intrinsic region is reached where carriers are thermally activated from valence band to the conduction band. The small activation energy observed may be attributed to the interaction between the electrons on the cations and π orbitals of ligand. This interaction will localize the π electrons charge on the ligand molecules^{17,18}.

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Table 1—Analytical, electrical and thermal data of polychelates

Compounds	% found (calcd)				Decomposition Temp (°C)	Activation Energy	Electrical conductivity (σ) ($\text{ohm}^{-1} \text{cm}^{-1}$)	Activation energy (E_a) (eV)
	C	H	N	M				
$\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2$	76.41 (77.03)	5.34 (5.94)	07.42 (7.56)	----	322	28.20	9.37×10^{-7}	
$[\text{VO}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)]_n$	68.52 (69.09)	5.05 (5.75)	9.73 (10.07)	11.99 (12.19)	380	24.14	7.50×10^{-7}	1.234
$[\text{Mn}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)\text{OAc}]_n$	61.11 (62.48)	4.32 (4.77)	6.00 (6.07)	11.22 (11.91)	374	19.80	2.37×10^{-8}	0.897
$[\text{Fe}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]_n$	61.03 (62.39)	4.72 (4.76)	6.01 (6.06)	11.09 (12.05)	263	18.17	7.50×10^{-8}	0.834
$[\text{Zr}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]_n$	61.90 (62.44)	4.03 (4.77)	5.92 (6.07)	19.01 (19.07)	352	18.63	4.00×10^{-9}	0.825
$[\text{Th}(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2]_n$	46.12 (47.80)	3.07 (3.65)	4.03 (4.65)	37.01 (38.05)	241	17.23	3.10×10^{-10}	0.469
$[\text{UO}_2(\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2)]_n$	44.48 (45.07)	3.01 (3.44)	3.98 (4.38)	37.02 (37.08)	247	14.87	6.10×10^{-10}	0.567

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A study on the solvation behaviour of BiBr₃ in MeCN, MeOH and DMF in presence of solvent ethanol

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Abstract

The nature of ion-solvent interaction involved in the system of the electrolyte BiBr₃ in MeCN, MeOH and DMF and the effect of addition of EtOH to it at different temperatures using electrical conductivity principle, is presented in this paper. Investigation showed the preferential solvation of the cation by the added ethanol in the case of MeCN+EtOH and DMF+EtOH mixtures. No preferential solvation by the ethanol is found in the case of MeOH+EtOH system. The limiting molar conductance of the electrolyte was determined by Kraus-Bray and Shedlovsky conductivity models. Limiting molar conductance increased in the order of EtOH<DMF<MeOH<MeCN, which is on the expected trend. Values of dissociation and association constants were also determined. The paper also reveals the energy of activation involved in the conductance process, thermodynamic parameters of association and solvation and the Walden product have been computed. From Fuoss-Accascina equation ion-pair formation constant K_p and ion triplet constant K_T were calculated and were used to support the variation in limiting conductance. Born relation was also verified. An attempt has been made to compute the solvation number using mobility method.

(**Keywords** : bismuth bromide/solvation behaviour/conductivity/Walden product)

Introduction

The measurement of conductance gives important information regarding ion-solvation^{1,2}. The study of variation of conductance with concentration, viscosity and dielectric constant provides satisfactory information not only about the behaviour of solutions but also of ion-solvation³. In recent years, there has been an increasing

interest in the behaviour of electrolytes in non-aqueous solvents with a view of investigating ion-ion and ion-solvent interactions under varied conditions⁴. The chemistry of bismuth is diverse⁵. Inorganic bismuth salts were the first compounds to be recognised for therapeutic utility⁵. Some compounds have been approved for human use under Federal Food, Drug and Cosmetic Act for more than 30 years⁵. There are no reports in literature regarding the conductivity behaviour of bismuth compounds except for some early investigations^{6,7}. From this laboratory, we have communicated the conductance behaviour of $\text{Bi}(\text{NO}_3)_3$ in water + DMF/DMSO⁸, and that of BiBr_3 in MeOH/MeCN + DMF⁹. As an extension of it, herein, we report the solvation behaviour of BiBr_3 in acetonitrile (MeCN), methanol (MeOH), dimethyl formamide (DMF), ethanol (EtOH) and their mixtures as a function of temperature.

Materials and Methods

Dimethyl formamide (DMF), ethanol (EtOH), methanol (MeOH) and acetonitrile (MeCN) were purified as mentioned in the literature^{10,11}. Commercially available BiBr_3 (NR Chem make, Mumbai) was used as such without further purification. Solution of BiBr_3 was prepared in pure solvents MeCN, MeOH, DMF and EtOH and also in the previously prepared mixtures of known composition (v/v) of MeCN/MeOH/DMF+EtOH. Since BiBr_3 undergoes hydrolysis to form BiOBr ¹², conductivity study is impossible in water. Conductance measurements were made with a digital direct reading conductivity meter (model C M. 180, Elico make) and a dip type calibrated 8 conductivity cell with cell constant 0.999 cm^{-1} . All the measurements were made in a thermostat maintained at the desired temperature $\pm 0.01^\circ\text{C}$. The instrument was standardised as described^{8,9}.

Results and Discussion

Limiting molar conductance:

The solution of BiBr_3 in various compositions of MeCN+EtOH, MeOH+EtOH and DMF+EtOH (v/v) were subjected to conductivity measurements at four different temperatures ($288\text{--}318 \pm 0.01 \text{ K}$). The conductivity meter gave the specific conductance of the solution directly which was used in the determination of molar conductance (Λ_m). Debye-Huckel-Onsager (DHO) equation was used to evaluate the limiting molar conductance at the initial stage. But the plot of Λ_m vs \sqrt{C} was non-linear and therefore did not proceed further to analyse the data by DHO equation.

Hence, Kraus - Bray equation related to 1:1 electrolyte was used since BiBr₃ undergoes ionisation in a solvent in the following manner¹³



The Kraus - Bray equation¹⁴ for such systems may be represented as

$$\frac{1}{\Lambda_m} = \frac{\Lambda_m C}{K_c \Lambda_m^{02}} + \frac{1}{\Lambda_m^0} \quad (2)$$

where Λ_m^0 is the limiting molar conductance, C is the concentration in molar and K_c is the dissociation constant. The Kraus-Bray plot was drawn for all the cases by taking $1/\Lambda_m$ along the Y -axis and $\Lambda_m C$ along the X -axis, and the plots were found to be linear. From the intercept and slope of the above linear plot (Fig. 1) the limiting molar conductance (Λ_m^0) and dissociation constant (K_c) were obtained and are shown in Table (1 and 2) respectively. The measurements were made at four different temperatures and at compositions of (v/v) MeCN/MeOH/DMF+EtOH (0, 20, 40, 60, 80 and 100% EtOH). The limiting molar conductance obtained are not absolute as it does not account for the effect of ionic mobility and activity coefficient on conductivity. Therefore, Shedlovsky model¹⁴ was tried, which accounts for the above facts, and hence expected to give absolute limiting conductance. The Shedlovsky equation may be represented as,

$$\frac{1}{S\Lambda_m^0} = \frac{f_{\pm}^2 S K_a C \Lambda_m}{\Lambda_m^{02}} + \frac{1}{\Lambda_m^{02}} \quad (3)$$

where

$$S = \left\{ \frac{\beta \sqrt{C \lambda_m}}{2 \lambda_m^{0 3/2}} + 1 + \frac{\beta^2 C \lambda_m}{4 \lambda_m^{0 3}} \right\}^2$$

$$\log f_{\pm} = \frac{-1.8246 \times 10^6 (C\alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.24 \times 10^8 R (C\alpha)^{1/2} / (\epsilon T)^{1/2}};$$

$$\beta = \frac{8.20 \times 10^5 \lambda_m^0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta(\epsilon T)^{1/2}}$$

$$\alpha = S\lambda_m/\lambda_m^0 ;$$

$$R = q = e^2/2\epsilon kT$$

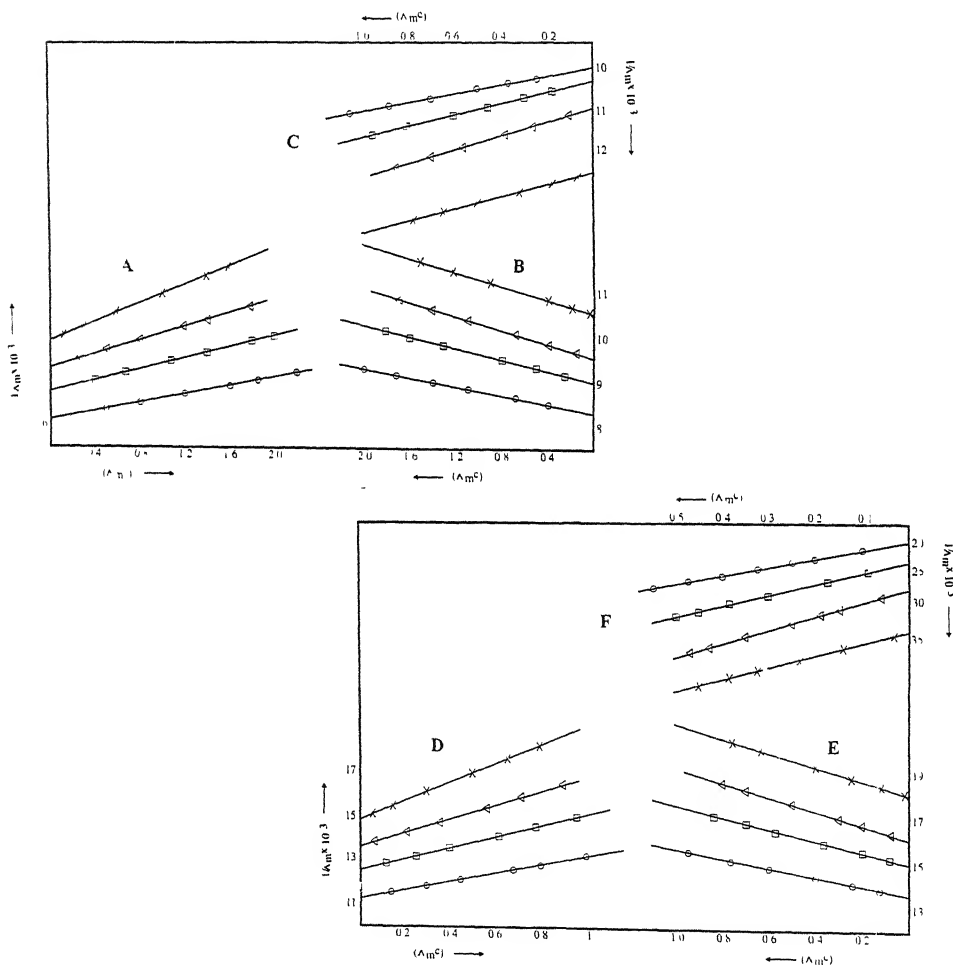


Fig 1-Plot of $1/\Lambda_m$ (ohm .cm² mol) V_s ($\Lambda_m C$) (mho cm⁻¹) for BiBr₃ in MeCN+EtOH system.

A. 100% MeCN, B . 80% MeCN, C. 60% MeCN, D. 40% MeCN, E. 20% MeCN,
F. 0% MeCN (100% EtOH), x 288K; Δ 11298 K; □ 0308 K, O 318 K.

where K_a is the association constant and f_{\pm} is the mean ionic activity coefficient of the electrolyte. From the intercept and slope of the linear plot of $1/S\Lambda_m$ vs $C\Lambda_m S f_{\pm}^2$, the limiting conductance and the association constant (K_a) were determined. These values are shown respectively in Tables 1 and 2. Λ_m^0 values obtained by both the models are almost the same.

[illegible]

Table 2- Experimental values of K_c and K_a for BiBr_3 in various compositions of MeCN/MeOH/DMF+EtOH at-

$T(\text{K})$	$K_c \times 10^{-2}$						K_a					
	0	20	40	60	80	100%	0	20	40	60	80	100%
MeCN + EtOH												
288	16.4	8.0	7.7	9.7	4.6	4.0	13.3	24.6	39.4	21.8	72.3	61.2
298	13.7	8.3	7.1	9.3	5.4	5.7	11.6	20.1	38.9	22.9	56.1	36.3
308	13.2	9.1	6.6	9.2	7.7	5.0	10.2	14.1	30.5	27.9	27.1	34.7
318	12.9	9.2	9.4	8.9	7.3	5.0	9.7	13.7	25.8	30.2	22.6	29.7
MeOH+EtOH												
288	2.9	5.4	5.9	6.3	2.9	4.0	76.3	33.1	29.6	60.4	66	61.2
298	3.2	4.5	3.9	4.2	3.2	5.7	75.1	43.4	41.3	65.1	77	36.3
308	3.5	3.8	3.4	4.0	3.8	5.0	64.3	61.7	48.6	70.9	62	34.7
318	4.1	3.4	3.7	4.1	4.4	5.0	43.5	67.6	61.5	75.6	48	29.7
DMF+EtOH												
288	6.1	7.1	4.6	2.8	2.0	4.0	30.1	21.0	31.5	66.4	110.3	61.2
298	5.6	6.8	4.4	2.7	2.4	5.7	33.4	29.4	34.0	64.5	78.9	36.3
308	5.2	6.2	4.2	3.1	2.6	5.0	34.3	31.8	41.1	61.5	78.5	34.7
318	4.9	5.8	4.1	3.6	2.7	5.0	37.5	31.2	36.7	43.2	62.4	29.7

From Table 1, it is clear that temperature enhances the conductivity for all compositions of MeCN/MeOH/DMF+EtOH. As expected, Λ_m^0 increased with increase in temperature in all the cases due to increase in thermal energy and mobility of ions. Inspection of Table 1 reveals that the limiting molar conductance in pure solvents varies in the order $\text{MeCN} > \text{MeOH} > \text{DMF} > \text{EtOH}$. According to Walden¹⁵ conductivity and viscosity are inversely related, i.e. higher the conductivity lower will be the viscosity. The viscosity of these solvents varies in the reverse order as

expected. Size of the solvent molecule is another reason for such variation in conductivity. The conductivity data clearly tells that acetonitrile is a better solvent and ethanol is the least preferred solvent as far as the dissolution and dissociation of BiBr₃ is concerned.

Table 1 also shows that addition of EtOH either to MeCN, MeOH or DMF decreases electrical conductivity continuously till the system becomes pure ethanol medium. The decrease in conductivity is sharp in the case of MeCN+EtOH and MeOH + EtOH, whereas the variation is small in the case of DMF+EtOH. Sharp decrease in conductivity is observed from 0 to 20% EtOH in the case of MeCN/MeOH+EtOH system. This trend is similar to the one observed in the case of addition of DMF to MeOH or MeCN⁹. This decrease hints at the increased ion-solvent interaction and also the solvent solvent interaction in the system. The addition of EtOH leads to solvent-solvent interaction forming increased solvent mixture molecular size and which is involved in solvation of the cation. Hence here we find both the ion-solvent and solvent-solvent interactions. The magnitude of solvent-solvent interaction can be determined by its density and viscosity value. They have been measured at different temperatures and reported in Table 3. Experimental density and viscosity values of pure solvents are in agreement with the literature values¹⁶ which are shown in bracket in Table 3. As is evident from Table 3 the viscosity increased with the increase in % compositions of EtOH and decreased with temperature in all the three cases of solvent mixtures. The presence of electrolyte will increase the viscosity further for any of the solvent mixtures or that of pure solvents. Therefore, conductance decreases from one composition to another at a given temperature. Sharp increase in viscosity is observed from 80% to 100% EtOH leading to sharp decrease in conductivity. From Table 1 it may also be inferred that EtOH preferentially solvates the ionic species of the electrolyte. In the case of DMF + EtOH, the viscosity decreases with increase in temperature, whereas the conductivity increases. But very marginal variation is observed from 0 to 80% EtOH indicating the least solvent-solvent interaction. But after 80% EtOH (which is ethanol rich region), the conductance decreases indicating higher ion-solvent interaction. That means, here it appears either no or negligible amount of solvent-solvent interaction. Probably, ethanol does not preferentially solvate the ionic species. The increased ion solvent interaction is found only after 60% EtOH.

Dissociation / Association Constants :



Table 3- Experimental values of density (d · gm/cm³) and viscosity (η milli poise) for MeCN/MeOH/DMF+EtOH at-

%EtOH	288K		298K		308K		318K	
	d	η	d	η	d	η	d	η
MeCN+EtOH								
0	0.7940	4.183	0.7899	3.652	0.7715	3.398	0.7607	3.225
				(3.55)				
20	0.7880	4.497	0.7800	3.933	0.7683	3.707	0.7600	3.400
40	0.7898	4.767	0.7819	4.107	0.7705	3.717	0.7603	3.422
60	0.7961	6.290	0.7870	5.126	0.7740	4.627	0.7645	4.081
80	0.7975	9.102	0.7875	7.461	0.7771	6.117	0.7692	5.636
100	0.8005	14.200	0.7934	11.400	0.7831	9.446	0.7739	7.655
MeOH+EtOH								
0	0.7856	6.244	0.7865	5.422	0.7772	4.742	0.7670	4.174
		(6.25)		(5.50)		(4.8)		(4.15)
20	0.8014	7.652	0.7916	6.321	0.7821	5.414	0.7725	4.851
40	0.8039	9.175	0.7969	7.535	0.7868	6.437	0.7784	5.703
60	0.8074	11.600	0.8019	9.183	0.7919	7.890	0.7835	6.643
80	0.8153	14.040	0.8091	11.300	0.7981	8.873	0.7892	7.641
100	0.8007	14.200	0.7934	11.400	0.7831	9.446	0.7739	7.655
DMF+EtOH								
0	0.9559	9.440	0.9443	7.937	0.9361	7.167	0.9283	6.413
				(7.960)				
20	0.9298	9.490	0.9190	7.966	0.9084	7.241	0.8998	6.499
40	0.8975	9.650	0.8895	8.037	0.8784	7.278	0.8703	6.559
60	0.8665	9.985	0.8581	8.384	0.8460	7.365	0.8372	6.660
80	0.8310	11.400	0.8248	9.099	0.8149	7.949	0.8070	7.349
100	0.8007	14.200	0.7934	11.400	0.7831	9.449	0.7739	7.655
				(11.30)		(9.30)		

The electrolyte BiBr₃ dissociates as shown in above equation. The calculated dissociation constant (K_c from Kraus-Bray) and association constant (K_a from Shedlovsky) values are shown in Table 2. K_c value decreased with the increase in temperature from 0-40% EtOH in DMF + EtOH system and increases there onwards. At 100% EtOH, it remained almost a constant. In the case of MeCN + EtOH system, the decrease in K_c is found at all compositions except at 20% and 80% EtOH with temperature. In MeOH+EtOH system increase is found at 0 and 80% EtOH and decrease at other % compositions with increase in temperature. It may be proposed that in some cases the system behaves like endothermic and in some other cases like exothermic process. K_c decreases from 0 to 80% except at 20% and 100% EtOH in DMF+EtOH system. The K_a increases from 0 to 80% in almost all the cases at a given temperature and finally decreased at 100% EtOH. Probably, the self association² of the solvent molecule brings about caged structure in the system capturing the conducting species of the electrolyte leading to the decrease in conductance. Similar trend is observed in the case of MeCN+EtOH system. The trend in variation of K_a at a given temperature in MeOH+EtOH system is quite different. Here K_a decreases for the initial addition of EtOH to MeOH (up to 40%) with a further increase in K_a till 80%. K_a values were used to calculate change in enthalpy, free energy and entropy of the association process. The K_c increased and K_a decreased in the order of MeOH<EtOH<DMF<MeCN.

Plot of $\log \Lambda_m$ vs $\log C$ was drawn on the basis of Fuoss equilibrium¹⁷, to prove that the association is predominating over dissociation process, which expects a slope of the linear plot around -0.5. In the present case slope value is more than -0.5. Therefore Fuoss-Kraus equation¹⁸ (eqn. 4) was used to prove further the presence of ion-pair association. where $g(c)$ is a factor which incorporates all inter ionic interaction terms K_p and K_T are the

$$\Lambda C g(C) \sqrt{C} = \frac{\Lambda_m^0}{K_p^{1/2}} + \frac{(\Lambda_m^0)^T K_T}{K_p^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_m^0} \right) C$$

ion pair and triple ion pair formation constants and $(\Lambda_m^0)^T$ is the limiting molar conductance of the triple ion. The values of ion pair formation constant K_p and ion triplet formation constant K_T were obtained respectively from the intercept and slope of the linear plot obtained from $\Lambda_m \sqrt{C}$ vs $[1 - \Lambda_m / \Lambda_m^0] C$. The value of K_p is found higher than K_T at all compositions at 298K in all the solvent mixtures (Table 4).

Moreover, a striking feature in this case is an increase in the value of K_p and decrease in the value of K_T from 20% to 80% EtOH. So the decrease in Λ_m^0 from 0-100% EtOH in all the cases can also be explained on the basis of K_p or K_T variation. This ideal trend is not observed in the case of pure solvents.

Table 4— Experimentally determined values of K_p and K_T for BiBr_3 in MeCN/MeOH/DMF+EtOH mixture at 25°C.

%EtOH	K_p			K_T		
	1	2	3	1	2	3
0	74.40	126.50	125.40	52.65	17.53	40.14
20	116.16	111.71	108.50	80.78	29.04	41.64
40	124.54	120.21	131.73	69.71	24.84	27.99
60	128.18	123.71	138.88	84.36	21.00	20.82
80	135.72	128.52	151.47	62.05	19.52	18.63
100	128.51	128.51	128.51	32.54	32.54	32.54
1 MeCN+EtOH mixture		2 MeOH+EtOH mixture		3. DMF+EtOH mixture		

Thermodynamic Parameters :

The energy of activation, E_a of the conducting rate process is calculated from the Arrhenius equation¹⁷, $\Lambda_m^0 = Ae^{-E_a/RT}$, where A is the frequency factor, R , the gas constant and T , the temperature on absolute scale. From the slope of the plot of $\log \Lambda_m^0$ vs $1/T$, E_a is calculated and are shown in Table 5. The variation in E_a with % composition of ethanol in anyone of the systems is almost on the expected trend. In the case of pure solvents, conductivity increases in the order, EtOH < DMF < MeOH < MeCN, where as the energy of activation increases in the reverse order. That means ideality is fully followed. ΔH_a , the enthalpy of association is calculated from the slope of the linear plot of $\log K_a$ vs $1/T$ in all the cases. It is found to be positive from 0 to 40% EtOH in DMF+EtOH mixture and 0 to 60% EtOH in MeOH+EtOH mixture indicating the endothermic behaviour of the system, but in other compositions including MeCN+EtOH, the ΔH_a is found to be negative and hence the system behaves like exothermic. ΔG_a , the free energy of association is calculated using the

Table 5- Calculated thermodynamic parameter values for BiBr₃ under varying compositions (v/v) of MeCN/MeOH/DMF+EtOH

Thermodynamic parameters	0	20	40	60	80	100%EtOH
MeCN+EtOH						
Ea(kJ mol ⁻¹)	6.4	6.6	7.1	7.4	7.5	11.5
ΔH _a (kJ mol ⁻¹)	-10.1	-15.3	-11.2	8.9	-29.2	-18.2
ΔS(K ⁻¹ kJ mol ⁻¹)*	-0.013	-0.027	-0.01	0.058	-0.069	-0.03
-ΔG (kJ mol ⁻¹)*	5.9	6.8	8.7	8.5	8.4	9.1
MeOH+EtOH						
Ea(kJ mol ⁻¹)	6.7	9.2	8.9	9.1	10.8	11.5
ΔH _a (kJ mol ⁻¹)	6.6	17.8	17.6	5.6	-19.1	-18.2
ΔS(K ⁻¹ kJ mol ⁻¹)*	0.057	0.092	0.090	0.053	-0.027	-0.029
-ΔG (kJ mol ⁻¹)*	10.4	10.6	9.9	10.9	10.6	9.1
DMF+EtOH						
Ea(kJ mol ⁻¹)	9.1	9.0	9.1	8.9	10.8	11.5
ΔH _a (kJ mol ⁻¹)	6.2	14.5	10.1	-4.8	-14.5	-18.2
ΔS(K ⁻¹ kJ mol ⁻¹)*	0.05	0.075	0.063	0.019	-0.011	-0.029
-ΔG (kJ mol ⁻¹)*	9.1	8.9	9.5	10.5	11.2	9.1

* at 308K

Walden Product :

Walden product¹⁹ relates molar conductance at infinite dilution (Λ_m^0) to viscosity (η_0) of the solvent as

$$\Lambda_m^0 \eta_0 = \frac{Ze_0 F}{6\pi r T} \quad (5)$$

where r is the Stoke's molecular radius. The product is calculated at all temperatures and % compositions for all the three cases. Walden product remains almost a constant within the experimental error either with increase in temperature or % compositions in DMF+EtOH system indicating the constancy in the Stoke's molecular radius. But in the case of MeCN+EtOH system, variation in conductivity has not been compensated by the variation in viscosity for a given temperature. Hence, Stoke's molecular radius does not remain the same. In MeOH+EtOH mixture the variation of Walden product is still different. It decreases with the increase in temperature at all compositions except at 20% EtOH. This decrease in the product from one composition to other is observed till about 40% EtOH with a later increase at all temperatures except at 318K. From the equation 5 it is clear that the plot of Walden product vs $1/r$, should be linear. This is true in the case of MeCN/MeOH+EtOH mixture.

Corrected Stoke's radii was calculated^{8,9} using equation 6 in all the solvent mixtures and the resulted values are given in Table 6.

$$r_i = \frac{ZF^2}{6\pi N \Lambda_m^0 \eta_0} + 0.0103 + r_y \quad (6)$$

where $r_y = 0.85 \text{ \AA}$ for dipolar unassociated solvents and $r_y = 1.13 \text{ \AA}$ applied to protic and other associated solvents, N is Avagadro number, Z is ionic charge, F is faraday constant and η_0 is the viscosity. There is a small variation in the radius with change in temperature as well as composition especially in the case of MeCN/MeOH+EtOH system.

Table 6— Corrected Stoke's radius (Å) of the conducting molecular species of BiBr₃ under varying compositions of MeCN/MeOH/DMF+EtOH at-

T/K	0	20	40	60	80	100%EtOH
MeCN+EtOH						
288	2.79	3.11	3.36	3.45	3.04	3.30
298	2.86	3.16	3.42	3.64	3.22	3.40
308	2.86	3.19	3.47	3.59	3.48	3.46
318	2.77	3.16	3.56	3.67	3.36	3.56
MeOH+EtOH						
288	2.63	2.87	2.80	2.71	2.61	3.30
298	2.65	2.88	2.75	2.72	2.67	3.40
308	2.69	2.80	2.82	2.76	2.92	3.46
318	2.76	2.77	2.77	2.81	2.94	3.56
DMF+EtOH						
288	3.24	3.20	3.13	3.36	3.35	3.30
298	3.31	3.25	3.26	3.43	3.66	3.40
308	3.31	3.30	3.23	3.50	3.61	3.46
318	3.24	3.24	3.23	3.49	3.50	3.56

Thermodynamics of Solvation :

Thermodynamic parameters, enthalpy (ΔH_{s-s}), free energy (ΔG_{s-s}) and entropy (ΔS_{s-s}) of solvation have been calculated using Born relation¹⁹

$$\Delta G_{s-s} = - \frac{N(Z_i e_0)^2}{r_i} \left(1 - \frac{1}{\epsilon} \right) \quad (7)$$

$$\Delta S_{s-s} = \frac{N(Z_i e_0)^2}{2r_i} \frac{1}{\epsilon^2} \frac{\delta \epsilon}{\delta T} \quad (8)$$

$$\Delta H_{s,s} = \Delta G_{s,s} + T\Delta S_{s,s} \quad (9)$$

where N_A is Avagadro Number, Z_i is the charge of the ion, e_0 , the electronic charge and r_i is the corrected Stoke's radius. $\Delta H_{s,s}$, calculated is found to be negative (Table 7) indicating the exothermic behavior of the solvation process. $\Delta G_{s,s}$ is found to be negative indicating the feasibility of the solvation process. The decrease in the value of $\Delta G_{s,s}$ with increase in temperature indicates that the species prefer to remain at lower temperature, where the stability of the species is higher. $\Delta G_{s,s}$ decreases with the increase in EtOH concentration in all the three cases of solvent mixtures in the positive direction. i.e. species try to be either in pure solvents or in solvent rich region. The plot of $-\Delta G_{s,s}$ vs $1/r_i$ was found linear indicating the verification of Born relation. $\Delta S_{s,s}$ is also negative but very small compared to $\Delta H_{s,s}$ or $\Delta G_{s,s}$. It decreased with the increase in the amount of ethanol at a given temperature or with increase in temperature for a given composition. That means, the disorderness and electrostriction increases with the increase in the amount of EtOH either to MeCN, MeOH or DMF.

Solvation Number - So :

The solvation number S_n of Bi^{3+} ion was calculated in four pure solvents at all temperatures using the relation,

$$S_n = \frac{\frac{4}{3}\pi r_i^3 - \frac{4}{3}\pi r_{cry}^3}{\frac{4}{3}\pi r_{sol}^3} \quad (10)$$

r_i is the Stoke's corrected radius, r_{cry} is the crystallographic radius and r_{sol} is the radius of the solvent molecule. r_{cry} for Bi^{3+} was obtained from the literature²⁰. The solvation number was found to be nearly one for all the solvents except in ethanol where it is nearing two (Table 8). So, species became bulky due to which mobility decreased and hence conductivity decreased from other solvents to ethanol for BiBr_3 species at a given temperature. This is what has been observed in the present case (Table 1).

Table 7- Thermodynamics of solvation for BiBr₃ in various compositions of MeCN/MeOH/DMF+EtOH at

T/K	0			20			40			60			80			100%EtOH		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
MeCN+EtOH																		
288	242	0.014	246	216	0.014	220	200	0.014	204	194	0.016	199	220	0.020	226	202	0.022	209
298	236	0.014	241	213	0.014	217	196	0.015	201	184	0.015	189	207	0.020	213	196	0.023	203
308	235	0.015	240	211	0.015	216	194	0.016	199	186	0.018	192	192	0.022	198	192	0.028	201
318	244	0.016	249	213	0.016	218	188	0.016	194	182	0.019	188	198	0.024	206	186	0.029	196
MeOH+EtOH																		
288	256	0.045	269	235	0.040	246	240	0.040	264	247	0.039	258	256	0.036	266	202	0.022	209
298	254	0.050	269	233	0.044	246	244	0.045	258	246	0.042	259	250	0.038	262	196	0.023	203
308	249	0.052	265	239	0.047	254	237	0.045	251	242	0.044	255	228	0.038	240	192	0.028	201
318	242	0.055	259	241	0.053	258	241	0.051	257	237	0.047	252	226	0.041	239	186	0.029	196
DMF+EtOH																		
288	208	0.026	215	211	0.027	219	214	0.027	222	199	0.025	206	199	0.024	206	202	0.022	209
298	204	0.028	212	207	0.029	216	206	0.028	214	195	0.026	203	183	0.023	190	196	0.023	203
308	204	0.033	214	204	0.033	214	207	0.033	217	191	0.030	201	185	0.025	192	192	0.028	201
318	208	0.038	220	207	0.037	219	207	0.037	219	191	0.033	202	190	0.028	199	186	0.029	196
1. - ΔG_{ss} (KJ mol ⁻¹)	2. - ΔS_{ss} (K ⁻¹ kJ mol ⁻¹)															3. - ΔH_{ss} (kJ mol ⁻¹)		

Table 8- Solvation number (S_n) of the cation of the species of BiBr_3 in MeCN, MeOH, DMF and EtOH at-

Solvent	S_n			
	288K	298K	308K	318K
MeCN	0.95	1.03	1.03	0.93
MeOH	1.01	1.04	1.09	1.19
DMF	1.06	1.12	1.12	1.06
EtOH	1.40	1.54	1.62	1.77

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Colorimetric determination of potassium using ferroin as reagent

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Abstract

A method for the determination of potassium is reported. Ferroin is used as a reagent in 6-10 N sulphuric acid medium which gives blue colour with potassium salt solution and the blue colour obtained has got 402 nm maximum absorbance where potassium is estimated colorimetrically in the range of 3.8-13.25 mg respectively.

(Keywords : colorimetric determination/potassium/ferroin)

Introduction

Several methods of determination of potassium have been reported mostly involving the instrumental methods viz., nephelometric, gasometric, flame photometric and spectrophotometric nature. The widely used flame photometric method requires special apparatus, sensitive detectors, photomultipliers and suffers the disadvantage of the interference of other elements which is sometimes contradictory in the determination of potassium.

The method for determination of potassium reported in this paper, is a simple and direct one. The potassium bromate in solution on reaction with ferroin in 6-10 N sulphuric acid medium gives blue colour and the optical density with reference to a known standard solution is measured and the amount is calculated.

Materials and Method

Reagents:

About 0.1 N solution of potassium bromate is prepared by weighing the required amount of Analar potassium bromate (supplied by B.D.H. Ltd., England) which has

been previously dried at 120°C for two hours and making up the solution to a known volume. The solution is standardised iodometrically¹.

0.025 M ferroin is prepared by dissolving 1.485 g of ortho-phenanthroline monohydrate in 100 mL of 0.025 M ferrous sulphate².

All other reagents used are of 'AnalaR' grade.

Colorimetric determination

Desired volume of 1:1 sulphuric acid is taken in each 25 mL volumetric flask to give an overall concentration of 6N. Different volumes of potassium bromate are added and mixed with 0.05 mL ferroin reagent. The blue colour developed is stable at room temperature. The maximum absorbance of the blue colour developed is at 402 nm. The Beers law curve obtained from known standard nitrate solution is given in Fig. 1. Typical results are given in Table 1.

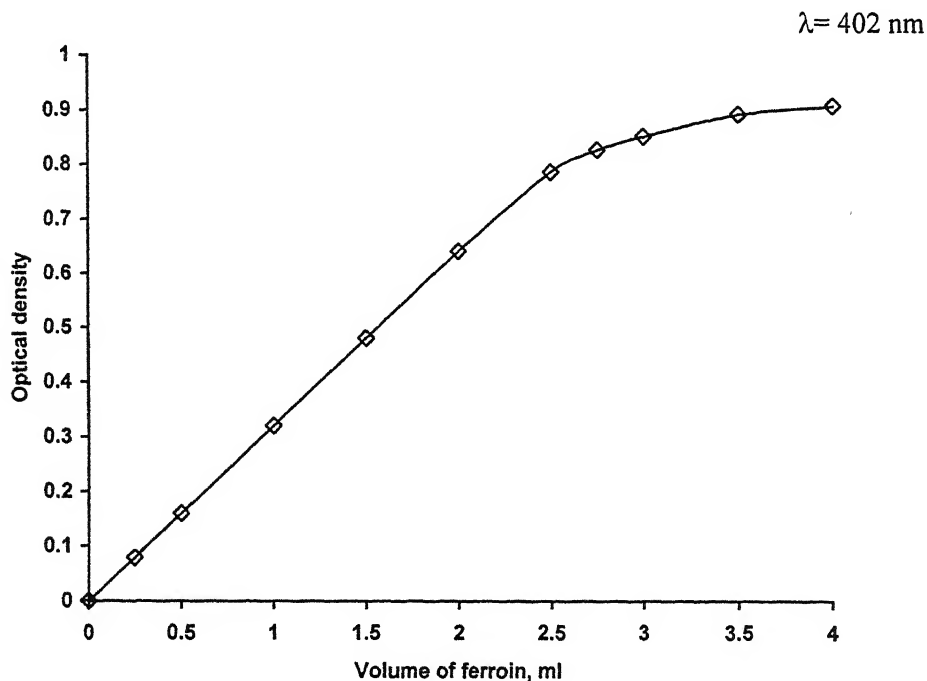


Fig. 1—Validity of Beer's law - Colorimetric determination of potassium with ferroin

Table 1—Colorimetric determination of potassium with ferroin Amount of potassium as K_2O , mg

Taken ¹	Found
3.82	3.804
7.361	7.358
10.645	10.648
13.250	13.258

Results and Discussion

It is found that the acidity should be in between 6-10 N for sulphuric acid for an immediate reaction. Below 6 N the colour development is rather slow and above 10 N the colour developed gets slowly discharged. It is observed that the colour attains maximum intensity within 3 min after mixing the reagent and remains stable for 48 h, if the reagent is in excess. In the colorimetric determination, the blue colour developed is stable at room temperature. It is observed that the blue colour developed has got maximum absorbance at 402 nm. The Beer's law is obeyed upto 13.2 mg of K_2O .

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Harvesting of a prey—predator fishery with low predator density

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Abstract

The paper deals with the combined harvesting of a prey–predator fishery with low predator density, the prey species obeying the logistic law of growth. The existence of a nontrivial steady state of the dynamical system describing the fishery is discussed. Both local and global stability of the steady state are studied. It is also examined whether the system possesses any limit cycle. Conditions for the existence of a bionomic equilibrium are established. The optimal harvest policy is discussed from the view point of control theory. The results are illustrated with the help of a numerical example. Sensitivity of the optimal solution to changes in different parameter values is then studied by using the same numerical example.

(Keywords) Harvesting/prey–predator fishery/bionomic equilibrium/optimal harvest policy)

1. Introduction

The problems related to harvesting of multispecies fisheries have drawn attention of researchers from time to time. It is always difficult, both theoretically and practically, to determine an optimal harvesting policy for the exploitation of a multispecies fishery. The difficulty actually lies in the construction of a realistic model of a multispecies system which leads to an analytically tractable optimal control problem. Carrying out dynamic optimization in problem involving more than two state variables is mathematically quite difficult. Moreover, reliable estimates of interaction coefficients are available for very few multispecies communities. In spite of these difficulties, researchers are engaged in the study of multispecies fisheries from mathematical view points. Mercer¹ made a survey of multispecies approaches to fishery management. Clark² devoted a separate chapter to this topic in his first book. In his second book, he discussed the prospects of bionomic modelling in the sphere of multispecies fisheries. Acknowledging the difficulties in multispecies modelling,

Clark³ observed: "It should be clear that no amount of bionomic modelling is going to solve the problems of multispecies fisheries. The best that can be hoped for is that a useful classification of the issues, and perhaps some insights into appropriate management principles will emerge." Clark² discussed an optimal equilibrium policy for combined harvesting of two ecologically independent species. Mesterton-Gibbons⁴ extended this model to discuss the optimal approach to equilibrium. Chaudhuri^{5,6} discussed a bionomic model of nonselective harvesting of two fish species competing for an external resource supporting their growth and survival. Saha Ray and Chaudhuri⁷ discussed a Lotka-Volterra prey-predator model with harvesting and environmental perturbations. Bionomic exploitation of a Lotka-Volterra prey-predator system was studied by Chaudhuri and Saha Ray⁸. The optimal policy for combined harvesting of a prey-predator community was also discussed by Mesterton-Gibbons⁹. In a recent paper, Mesterton-Gibbons¹⁰ reconsidered the problems of Chaudhuri^{5,6} to derive its optimal solution.

In the present paper, we have adopted a model similar to that of Smith¹¹ to describe the development of a prey-predator community in a fishery. Smeach and Rust¹² made a stochastic study of the model of Smith¹¹ using the mean-square theory of stochastic differential equations. However, they were not concerned with harvesting and as a consequence, they had nothing to do with bionomic analysis. We considered joint harvesting of a prey-predator community whose biological development is governed by a Smith type model¹¹. The dynamical behaviour of the system is first studied. It is shown that a nontrivial steady state exists under certain conditions which are amenable to interpretations relevant to the model. Both local and global stability of this steady state are then discussed; existence of limit cycles is also examined. Bionomic equilibrium of the system is next discussed. We then study the optimal harvesting policy from a control-theoretical view point. A numerical example is taken up to illustrate the results. Sensitivity of the optimal solution to changes in the values of different parameters is also examined.

2. Statement of the Problem

Let us consider two competing fish population whose growth obey the following dynamical system :

$$\begin{aligned}\frac{dx_1}{dt} &= r_1 x_1 \left(1 - \frac{x_1}{k}\right) - \alpha x_1 x_2 = F(x_1, x_2) \\ \frac{dx_2}{dt} &= \frac{r_2 x_1 x_2}{k} - \beta x_2 = G(x_1, x_2)\end{aligned}\tag{1}$$

where r_1 , r_2 , α , β , k are all positive constants.

Here $x_1(t)$ = the size or biomass of the prey population at time t ,

$x_2(t)$ = the size or biomass of predator population at time t ,

r_1 = biotic potential of the prey,

r_2 = the maximum reproductive rate of the predator,

α = the rate at which the prey species is removed due to predation effects,

β = per capita death rate of the predator,

k = the carrying capacity of the prey population.

The crowding effect term (due to intra-specific competition) $\frac{r_1 x_1^2}{k}$ is present in the first equation and it is absent in the second equation of the model. This indicates that the predator density is low; the predator species dies out exponentially in the absence of the prey.

Equations of the type (1) have been used by Smith¹¹ to model the development of a prey–predator community with low predator density.

We now assume that both the species are subjected to a combined harvesting effort governed by the differential equations:

$$\begin{aligned}\frac{dx_1}{dt} &= r_1 x_1 \left(1 - \frac{x_1}{k}\right) - \alpha x_1 x_2 - q_1 E x_1 \\ \frac{dx_2}{dt} &= \frac{r_2 x_1 x_2}{k} - \beta x_2 - q_2 E x_2\end{aligned}\tag{2}$$

where q_1 , q_2 are the catchability coefficients of the two species and E denotes the effort devoted to their combined harvesting. We intend to study the characteristics of the exploited prey–predator fish species described by the dynamical system (2) and also some economic implications of the harvesting policy.

3. Dynamical Behaviour

(A) *Steady state :*

The steady states of the system of equations (2) are

$$P_0(0, 0), P_1(x_1^*, x_2^*), P_2(\bar{x}_1, \bar{x}_2)$$

$$\text{where } x_1^* = \frac{k}{r_1}(r_1 - q_1 E), \quad (3)$$

$$x_2^* = 0, \quad (4)$$

$$\bar{x}_1 = \frac{k(\beta + q_2 E)}{r_2}, \quad (5)$$

$$\text{and } \bar{x}_2 = \{r_1(r_2 - \beta) - E(r_1 q_2 + r_2 q_1)\} / \alpha r_2. \quad (6)$$

The nontrivial steady states of the system (2) are

$$P_1(x_1^*, x_2^*) \text{ and } P_2(\bar{x}_1, \bar{x}_2).$$

$$\text{For } x_1^* > 0, \text{ we must have from (3), that } E < \frac{r_1}{q_1}. \quad (7)$$

From (5), we have \bar{x}_1 is always positive.

$$\text{It is obvious that } r_2 > \beta \quad (8)$$

$$\text{and therefore, } \bar{x}_2 > 0 \text{ iff } r_1(r_2 - \beta) > E(r_1 q_2 + r_2 q_1) \quad (9)$$

For the unexploited system ($E = 0$), the nontrivial steady states \bar{P}_1 and \bar{P}_2 become $\bar{P}_1(k, 0)$ and $\bar{P}_2\left(\frac{k\beta}{r_2}, \frac{r_1(r_2 - \beta)}{\alpha r_2}\right)$, $r_2 > \beta$.

These results perfectly agree with those of Smeach and Rust¹² for $\beta = 1$. Comparing P_2 with \bar{P}_2 , we find that the combined harvesting effort increases the equilibrium level of the prey, but decreases that for the predator. Comparing \bar{P}_1 with P_1 , it is observed that, in the absence of the predator, the harvesting effort decreases the prey level.

The condition (9) may be written as :

$$0 < \frac{r_1}{q_1} + \frac{r_2}{q_2} < \frac{r_1(r_2 - \beta)}{Eq_1q_2}. \quad (10)$$

In fishery literature, the ratio of biotic potential (r) to the catchability coefficient (q) of a species is called its BTP (biotechnical productivity)². Thus, $\frac{r_1}{q_1}$ and $\frac{r_2}{q_2}$ are the prey-BTP and the predator-BTP respectively. Condition (10) thus establishes $\frac{r_1(r_2 - \beta)}{Eq_1q_2}$ as the maximum value of the sum of these two BTP's. When the sum of these BTP's attains the maximum value, the predator population is extinct ($\bar{x}_2 = 0$). On the other hand condition (7) shows that, in the absence of predators, if the harvesting effort is equal to the prey-BTP, the prey population is extinct ($x_1^* = 0$) and P_1 coincides with P_0 .

Condition (9) may also be rewritten as,

$$0 < E < \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}. \quad (11)$$

Condition (11) defines $E_{\max} = \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}$ as the upper limit of the level of harvesting effort. We must have $0 < E < E_{\max}$ for the existence of positive steady states of both the prey and the predator. If $E = E_{\max} = \frac{r_1(r_2 - \beta)}{r_1q_2 + r_2q_1}$ the predator population becomes extinct ($\bar{x}_2 = 0$).

(B) Local stability

The variational matrix of the system (2) is

$$V(x_1, x_2) = \begin{bmatrix} r_1 - \frac{2r_1x_1}{k} - \alpha x_2 - q_1E & -\alpha x_1 \\ \frac{r_2x_2}{k} & \frac{r_2x_1}{k} - \beta - q_2E \end{bmatrix}.$$

$$\text{At } P_0(0, 0), V(0, 0) = \begin{bmatrix} r_1 - q_1E & 0 \\ 0 & -(\beta + q_2E) \end{bmatrix}.$$

Therefore, the eigenvalues of the variational matrix of the system (2) at $P_0(0, 0)$ are $r_1 - q_1E$ and $-(\beta + q_2E)$.

If the prey-BTP $\frac{r_1}{q_1} > E$, then the eigenvalue $(r_1 - q_1E)$ is positive while the other eigenvalue is obviously negative. In this case, the equilibrium point $P_0(0, 0)$ is a saddle point.

On the other hand, if $\frac{r_1}{q_1} < E$, then both the eigenvalues being real and negative, P_0 is a stable node. However, $\frac{r_1}{q_1} < E$, makes both x_1^* and \bar{x}_2 negative. In that case, no nontrivial steady state exists. We, therefore, discard the case $\frac{r_1}{q_1} < E$ and accept (7) as the basic condition for the existence of a nontrivial steady state.

$$\begin{aligned} \text{At } P_1(x_1^*, x_2^*), V(x_1^*, x_2^*) &= \begin{bmatrix} -\frac{r_1x_1^*}{k} & -\alpha x_1^* \\ 0 & \frac{r_2x_1^*}{k} - \beta - q_2E \end{bmatrix} \\ &= \begin{bmatrix} -(r_1 - q_1E) & -\frac{\alpha k}{r_1}(r_1 - q_1E) \\ 0 & \frac{r_2}{r_1}(r_1 - q_1E) - \beta - q_2E \end{bmatrix}. \end{aligned}$$

The eigenvalues at $P_1(x_1^*, x_2^*)$ are

$$-(r_1 - q_1 E) \text{ and } \frac{r_2}{r_1}(r_1 - q_1 E) - \beta - q_2 E.$$

Now $-(r_1 - q_1 E) < 0$ by (7).

$$\begin{aligned} \text{If } \frac{r_2}{r_1}(r_1 - q_1 E) - \beta - q_2 E &= \frac{r_2(r_1 - q_1 E) - r_1\beta - q_2 E r_1}{r_1} \\ &= \frac{1}{r_1} \{r_1(r_2 - \beta) - E(q_2 r_1 + r_2 q_1)\} < 0, \end{aligned}$$

then P_1 is a stable node. However, \bar{x}_2 becoming negative in this case, P_2 does not exist.

Thus, P_1 is the only nontrivial steady state and it is a stable node when the reverse of the inequality (9) holds. When P_2 also exists, the inequality (9) holds and the second eigen value becomes positive; as a result P_1 becomes a saddle point.

The variational matrix of the system (2) at $P_2(\bar{x}_1, \bar{x}_2)$ is

$$V(\bar{x}_1, \bar{x}_2) = \begin{bmatrix} -\frac{r_1 \bar{x}_1}{k} & -\alpha \bar{x}_1 \\ \frac{r_2 \bar{x}_2}{k} & 0 \end{bmatrix}.$$

The eigen values $\lambda_i (i = 1, 2)$ of the system (2) at $P_2(\bar{x}_1, \bar{x}_2)$ are the roots of the following quadratic equation in λ :

$$\begin{vmatrix} -\frac{r_1 \bar{x}_1}{k} - \lambda & -\alpha \bar{x}_1 \\ \frac{r_2 \bar{x}_2}{k} & -\lambda \end{vmatrix} = 0.$$

$$\text{or, } k\lambda^2 + r_1 \bar{x}_1 \lambda + \alpha r_2 \bar{x}_1 \bar{x}_2 = 0.$$

(12)

Discriminant of the equation (12) is

$$D = r_1^2 \bar{x}_1^2 - 4\alpha k r_2 \bar{x}_1 \bar{x}_2.$$

$$\text{In equation (12), sum of the roots} = -\frac{r_1 \bar{x}_1}{k} < 0$$

$$\text{and product of the roots} = \frac{\alpha r_2 \bar{x}_1 \bar{x}_2}{k} > 0.$$

Therefore, the roots are either both real and negative or complex conjugates with negative real parts.

The eigen values are real or complex depending on $D > 0$ or < 0 which implies

$$E > \text{or} < \frac{4r_1 r_2 (r_2 - \beta) - r_1^2 \beta}{4r_2 (q_1 r_2 + q_2 r_1) + q_2 r_1^2} = \bar{E} \text{ (say)} \quad (13)$$

This result perfectly agrees with that of Smeach and Rust¹² for $\beta = 1$ in the case of an unexploited system ($E = 0$). Combining (13) with the condition on E_{\max} for the existence of the steady state ($\bar{x}_1 \neq 0, \bar{x}_2 \neq 0$), we find that

$$(a) \quad \bar{E} < E < E_{\max}$$

when the eigenvalues are real and negative and

$$(b) \quad 0 < E < \text{Min}(E_{\max}, \bar{E})$$

when the eigenvalues are complex conjugates with negative real parts.

When the eigenvalues of the system (2) are both real and negative, the non-trivial critical point $P_2(\bar{x}_1, \bar{x}_2)$ will be an asymptotically stable node. On the other hand, the critical point P_2 will be a stable focus when the eigenvalues are complex conjugates with negative real parts.

Thus, when both P_1 and P_2 exist, i.e. when both the inequalities (7) and (9) hold simultaneously, we find that

- (i) P_0 is a saddle point;
- (ii) P_1 is a saddle point;
- (iii) P_2 is a stable node or a stable focus depending on the value of the effort E .

By this eigenvalue analysis, we get the behaviour of the dynamical system (2) only in the neighbourhood of the critical points.

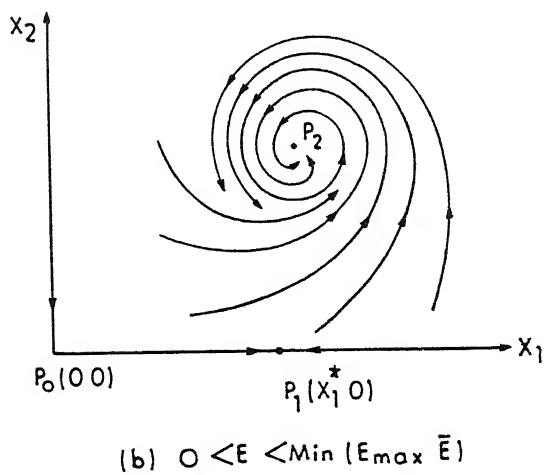
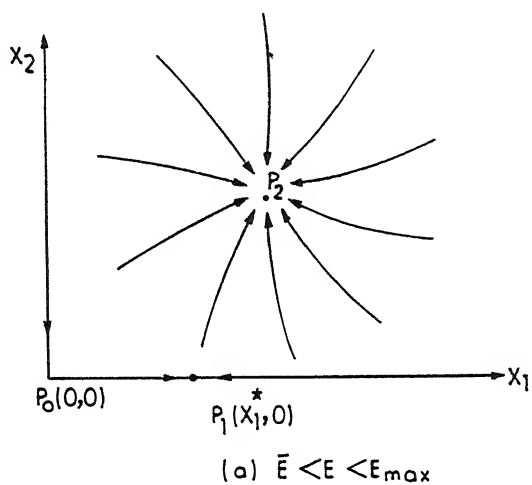


Fig 1

(C) *Limit cycle :*

The system may have a limit cycle, we now examine the possibility of existence of a limit cycle of the non-linear system (2) by using Bendixon–Dulac test in the form suggested by Clark² (p.208).

Writing the dynamical system (2) in the form

$$\begin{aligned}\frac{dx_1}{dt} &= x_1(a_1x_1 + b_1x_2 + c_1) = f(x_1, x_2) \\ \frac{dx_2}{dt} &= x_2(a_2x_1 + b_2x_2 + c_2) = g(x_1, x_2)\end{aligned}\tag{14}$$

where $a_1 = -\frac{r_1}{k}$, $b_1 = -\alpha$, $c_1 = r_1 - q_1E$,

$$a_2 = \frac{r_2}{k}, \quad b_2 = 0, \quad c_2 = -(\beta + q_2E).$$

We find $\Delta = a_1b_2 - a_2b_1 = \frac{\alpha r_2}{k} \neq 0$

and $a_1c_2(b_1 - b_2) + b_2c_1(a_2 - a_1) = \frac{-\alpha r_1(\beta + q_2E)}{k} \neq 0$

$$\sigma = \frac{b_2(a_2 - a_1)}{\Delta} = 0, \quad \tau = \frac{a_1(b_1 - b_2)}{\Delta} = \frac{r_1}{r_2}.$$

Introducing the function

$$B(x_1, x_2) = x_1^{\sigma-1} x_2^{\tau-1} = x_1^{-1} x_2^{\frac{r_1}{r_2}-1},$$

we find that $\frac{\partial}{\partial x_1}(Bf) + \frac{\partial}{\partial x_2}(Bg) = -\frac{r_1}{r_2} x_1^{-1} x_2^{\frac{r_1}{r_2}-1} (\beta + q_2E) < 0$

always in a simply connected region D in the x_1 - x_2 plane.

Hence the expression

$$\frac{\partial}{\partial x_1}(Bf) + \frac{\partial}{\partial x_2}(Bg) \text{ does not change sign in } D.$$

Hence the system (2) does not possess limit cycles.

(D) *Global stability* :

We now examine the global stability of the dynamical system (2). We have already noted that this system has a unique positive equilibrium at $P_2(\bar{x}_1, \bar{x}_2)$ provided the conditions (8) and (9) hold. The prey-density having a carrying capacity and the predator density being low, we may assume that the solutions of the dynamical system (2) are eventually uniformly bounded in a finite region B in the (x_1, x_2) phase plane and hence all solutions of (2) starting in R_2^+ enter into the region B . We shall now prove that the interior equilibrium $P_2(\bar{x}_1, \bar{x}_2)$ is globally asymptotically stable in the Lyapunov sense in the region B .

We define a Lyapunov function

$$V(x_1, x_2) = x_1 - \bar{x}_1 - \bar{x}_1 \ln \left(\frac{x_1}{\bar{x}_1} \right) + d \left\{ x_2 - \bar{x}_2 - \bar{x}_2 \ln \left(\frac{x_2}{\bar{x}_2} \right) \right\}$$

where d is a suitable constant to be determined in the subsequent steps.

Obviously V is a positive definite function in the region B except at $P_2(\bar{x}_1, \bar{x}_2)$ where it vanishes.

$$\text{Further } \lim_{(x_1, x_2) \rightarrow (0, 0)} V(x_1, x_2) = \lim_{(x_1, x_2) \rightarrow (\infty, \infty)} V(x_1, x_2) = \infty$$

The derivative of V along the solution of (2) is

$$\begin{aligned}
V(x_1, x_2) &= \frac{\dot{x}_1}{x_1}(x_1 - \bar{x}_1) + d \frac{\dot{x}_2}{x_2}(x_2 - \bar{x}_2) \\
&= (x_1 - \bar{x}_1) \left\{ r_1 \left(1 - \frac{x_1}{k} \right) - \alpha x_2 - q_1 E \right\} + d(x_2 - \bar{x}_2) \left(\frac{r_2 x_1}{k} - \beta - q_2 E \right) \\
&= (x_1 - \bar{x}_1) \left\{ \left[r_1 \left(1 - \frac{x_1}{k} \right) - \alpha x_2 - q_1 E \right] - \left[r_1 \left(1 - \frac{\bar{x}_1}{k} \right) - \alpha \bar{x}_2 - q_1 E \right] \right\} \\
&\quad + d(x_2 - \bar{x}_2) \left\{ \left(\frac{r_2 x_1}{k} - \beta - q_2 E \right) - \left(\frac{r_2 \bar{x}_1}{k} - \beta - q_2 E \right) \right\} \\
&= (x_1 - \bar{x}_1) \left\{ -\frac{r_1}{k}(x_1 - \bar{x}_1) - \alpha(x_2 - \bar{x}_2) \right\} + \frac{dr_2}{k}(x_2 - \bar{x}_2)(x_1 - \bar{x}_1) \\
&= -\frac{r_1}{k}(x_1 - \bar{x}_1)^2 + \left(\frac{dr_2}{k} - \alpha \right) (x_1 - \bar{x}_1)(x_2 - \bar{x}_1) \\
&= -\frac{r_1}{k}(x_1 - \bar{x}_1)^2 < 0 \text{ provided } d = \frac{k\alpha}{r_2}.
\end{aligned}$$

Clearly $\dot{V} = 0$ when $x_1 = \bar{x}_1$. On the set $\{(x_1, x_2) : x_1 = \bar{x}_1\}$ the only invariant set is $\{(\bar{x}_1, \bar{x}_2)\}$. Hence by Lasalle's invariance principle¹³, $P_2(\bar{x}_1, \bar{x}_2)$ is globally asymptotically stable. As a consequence of the global asymptotic stability of the equilibrium point P_2 in the subspace B of R_2^+ , it again follows that the system (2) has no limit cycles.

4. Bionomic Equilibrium

Let, c = fishing cost per unit effort,

p_1 = price per unit bio-mass of the prey species

and p_2 = price per unit bio-mass of the predator species.

The economic rent (net revenue) at any time is given by

$$\pi(x_1, x_2, E) = p_1 q_1 E x_1 + p_2 q_2 E x_2 - cE.$$

We find that, $\dot{x}_1 = 0 = \dot{x}_2$ yield the results

$$\frac{r_2 x_1}{k q_2} = \frac{\beta}{q_2} + E, \quad (15)$$

$$\text{and} \quad \frac{\alpha r_2 x_2}{r_1 q_2 + r_2 q_1} = \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} - E. \quad (16)$$

Eliminating E , we find that, the nontrivial equilibrium point of the exploited system (2) occurs at a point on the line

$$\frac{r_2 x_1}{k q_2} + \frac{\alpha r_2 x_2}{r_1 q_2 + r_2 q_1} = \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1}. \quad (17)$$

The biological equilibrium line (17) meets the x_1 - axis and x_2 -axis at $(\tilde{x}_1, 0)$ and $(0, \tilde{x}_2)$ respectively where

$$\tilde{x}_1 = \frac{k q_2}{r_2} \left\{ \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} \right\} = \frac{k(\beta q_1 + r_1 q_2)}{r_1 q_2 + r_2 q_1} > 0$$

$$\text{and} \quad \tilde{x}_2 = \frac{(r_1 q_2 + r_2 q_1)}{\alpha r_2} \left\{ \frac{\beta}{q_2} + \frac{r_1(r_2 - \beta)}{r_1 q_2 + r_2 q_1} \right\} = \frac{\beta q_1 + r_1 q_2}{\alpha q_2} > 0.$$

The bionomic equilibrium $(x_{1\infty}, x_{2\infty})$ of the model (2) is given by (17) together with the condition

$$\pi = (p_1 q_1 x_1 + p_2 q_2 x_2 - c)E = 0 \quad (18)$$

As long as $(p_1 q_1 x_1 + p_2 q_2 x_2 - c) < 0$ for all points on the equilibrium line (17), the species remain unexploited because the fishery fails to produce any positive economic revenue.

The three situations that may arise with respect to the intersections of the lines (17) and (18) are given below in corresponding figures.

In Fig. 2(a), positive bionomic equilibrium exists for both the species.

In Figs. 2(b) and 2(d), the zero-profit line and the bionomic equilibrium line intersect in the second quadrant of the phase plane where $x_{1\infty}$ is negative. Hence no bionomic equilibrium exists in these cases. Similarly, no bionomic equilibrium exists in Figs. 2(c) and 2(e) also in which the two lines intersect in the fourth quadrant where $x_{2\infty}$ is negative.

In Figs. 2(b) and 2(c), the biological equilibrium line lies above the economic indifference line. Thus there is an economic advantage in both the cases whatever the biological equilibrium point is. It is a case of economic equilibrium only which is attained before the biological steady state is reached.

In Figs. 2(d) and 2(e), the economic indifference line lies above the biological equilibrium line. As a result, the fishermen would continue to harvest until the zero-profit lines $\pi = 0$ is reached without caring for biological equilibrium. Thus, this is also a case of economic equilibrium only occurring beyond the biological steady state.

Solving (17) and (18), we get,

$$x_{1\infty} = \frac{k\{\alpha c - p_2(r_1 q_2 + \beta q_1)\}}{\{\alpha k p_1 q_1 - p_2(r_1 q_2 + r_2 q_1)\}} \quad (19)$$

$$x_{2\infty} = \frac{k p_1 q_1 (r_1 q_2 + q_1 \beta) - c(r_1 q_2 + r_2 q_1)}{\alpha k p_1 q_1 q_2 - p_2 q_2 (r_1 q_2 + r_2 q_1)} \quad (20)$$

Thus $x_{1\infty}$ and $x_{2\infty}$ are respectively given by (5) and (6) in which E is to be replaced by the bionomic effort level E_∞ . Using the open-access condition $\pi(E_\infty) = 0$, we get

$$E_\infty = \frac{\alpha c r_2 - \alpha \beta p_1 q_1 k - p_2 q_2 r_1 (r_2 - \beta)}{\alpha p_1 q_1 q_2 k - p_2 q_2 (r_1 q_2 + r_2 q_1)}.$$

Now $x_{1\infty} > 0$ provided either of the following conditions holds :

$$(A) \quad p_2 > \max \left\{ \frac{\alpha c}{r_1 q_2 + \beta q_1}, \frac{\alpha k p_1 q_1}{r_1 q_2 + r_2 q_1} \right\},$$

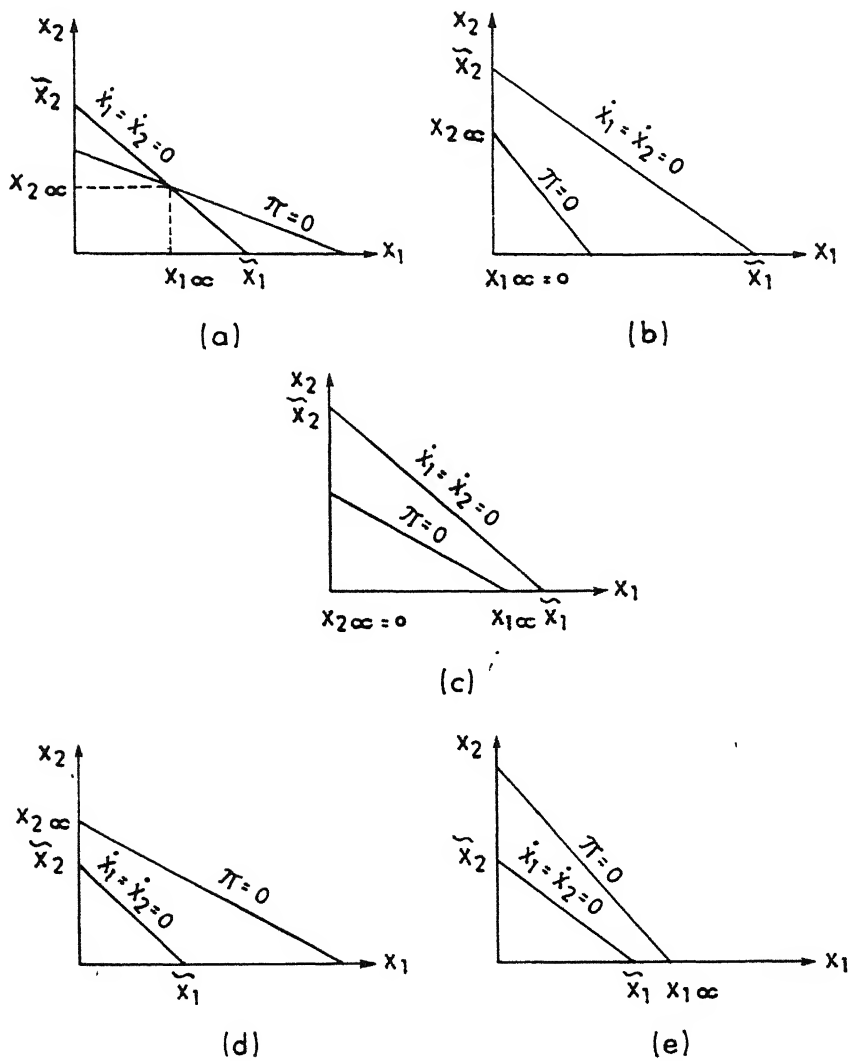


Fig. 2— Biodynamic equilibrium of the prey-predator fishery

(a) Non-extinction, (b) and (d) Extinction of prey, (c) and (e) Extinction of predator

$$(B) \ p_2 < \min \left\{ \frac{\alpha c}{r_1 q_2 + \beta q_1}, \frac{\alpha k p_1 q_1}{r_1 q_2 + r_2 q_1} \right\}.$$

Similarly, $x_{2\infty} > 0$ provided that

$$(C) \ \frac{r_1}{q_1} + \frac{r_2}{q_2} > \max \left\{ \frac{k p_1}{c} \left(r_1 + \frac{\beta q_1}{q_2} \right), \frac{\alpha k p_1}{p_2 q_2} \right\},$$

$$(D) \ \frac{r_1}{q_1} + \frac{r_2}{q_2} > \min \left\{ \frac{k p_1}{c} \left(r_1 + \frac{\beta q_1}{q_2} \right), \frac{\alpha k p_1}{p_2 q_2} \right\} \text{ holds.}$$

When either (A) or (B) and (C) or (D) hold simultaneously, both the species co-exist in bionomic equilibrium. When either (A) or (B) holds and neither (C) nor (D) holds, the predator species faces extinction in the bionomic equilibrium; the bionomic equilibrium of the fishery is supported by the prey species only. Similarly when either (C) or (D) holds and neither (A) nor (B) holds, the prey species faces extinction in the bionomic equilibrium and as a consequence, the predator population also is eventually driven to extinction.

5. Optimal Harvest Policy :

Our objective is to maximize the present value J of a continuous-time stream of revenues given by

$$J = \int_0^{\infty} e^{-\delta t} \{p_1 q_1 x_1 + p_2 q_2 x_2 - c\} E(t) dt \quad (21)$$

where δ denotes the instantaneous annual rate of discount.

We intend to maximize (21) subject to the state equations (2).

The Hamiltonian for the problem is given by

$$H = e^{-\delta t} \left\{ p_1 q_1 x_1 + p_2 q_2 x_2 - c \right\} E(t) + \lambda_1 \left\{ r_1 x_1 - \frac{r_1 x_1^2}{k} - \alpha x_1 x_2 - q_1 E x_1 \right\} \\ + \lambda_2 \left\{ \frac{r_2 x_1 x_2}{k} - \beta x_2 - q_2 E x_2 \right\} \quad (22)$$

where $\lambda_1(t)$ and $\lambda_2(t)$ are the adjoint variables.

The adjoint equations are

$$\frac{d\lambda_1}{dt} = -\frac{\partial H}{\partial x_1} = -e^{-\delta t} p_1 q_1 E - \lambda_1 (F_{x_1} - q_1 E) - \lambda_2 G_{x_1} \quad (23)$$

$$\text{and} \quad \frac{d\lambda_2}{dt} = -\frac{\partial H}{\partial x_2} = -e^{-\delta t} p_2 q_2 E - \lambda_1 F_{x_2} - \lambda_2 (G_{x_2} - q_2 E). \quad (24)$$

We consider the optimal equilibrium solution of the given problem so that, we may write

$$E = \frac{F(x_1, x_2)}{q_1 x_1} = \frac{G(x_1, x_2)}{q_2 x_2}. \quad (25)$$

Equations (23) and (24) can be written as

$$\frac{d\lambda_1}{dt} = -e^{-\delta t} p_1 q_1 E - \lambda_1 \left(r_1 - \frac{2r_1 x_1}{k} - \alpha x_2 - q_1 E \right) - \frac{\lambda_2 r_2 x_2}{k} \quad (26)$$

$$\text{and} \quad \frac{d\lambda_2}{dt} = -e^{-\delta t} p_2 q_2 E + \lambda_1 \alpha x_1 - \lambda_2 \left(\frac{r_2 x_1}{k} - \beta - q_2 E \right). \quad (27)$$

$$\text{Equation (25) implies } r_1 - \frac{r_1 x_1}{k} - \alpha x_2 - q_1 E = 0 \quad (28)$$

$$\text{and } \frac{r_2 x_1}{k} - \beta - q_2 E = 0. \quad (29)$$

Using (28) and (29) in (26) and (27) we get

$$\frac{d\lambda_1}{dt} = -e^{-\delta t} p_1 q_1 E + \frac{\lambda_1 r_1 x_1}{k} - \frac{\lambda_2 r_2 x_2}{k} \quad (30)$$

$$\text{and } \frac{d\lambda_2}{dt} = -e^{-\delta t} p_2 q_2 E + \lambda_1 \alpha x_1. \quad (31)$$

Differentiating (30) with respect to t and using (31), we get,

$$\frac{d^2 \lambda_1}{dt^2} - \frac{r_1 x_1}{k} \frac{d\lambda_1}{dt} + \frac{r_2 \lambda_1 \alpha x_1 x_2}{k} = E e^{-\delta t} \left(\delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k} \right). \quad (32)$$

Auxilliary equation of (32) is

$$m^2 - \frac{r_1 x_1}{k} m + \frac{r_2 \alpha x_1 x_2}{k} = 0 \quad (33)$$

If m_1 and m_2 be the roots of the quadratic equation (33), then,

$$m_1 + m_2 = \frac{r_1 x_1}{k} > 0, \quad m_1 m_2 = \frac{r_2 \alpha x_1 x_2}{k} > 0.$$

Therefore, the roots of the equation (33) are both real and positive or complex conjugates with positive real parts.

Case (i) : When both the roots are real and unequal, the general solution of (32) is

$$\begin{aligned} \lambda_1(t) &= A_1 e^{m_1 t} + B_1 e^{m_2 t} + \frac{M_1}{N_1} e^{-\delta t} \\ \Rightarrow \lambda_1 e^{\delta t} &= A_1 e^{(m_1 + \delta)t} + B_1 e^{(m_2 + \delta)t} + \frac{M_1}{N_1} \end{aligned}$$

$$\text{where } M_1 = E \left(\delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k} \right),$$

$$N_1 = \delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 \alpha x_1 x_2}{k}$$

and A_1, B_1 are arbitrary constants.

Thus the shadow price $e^{\delta t} \lambda_1(t)$ remains bounded as $t \rightarrow \infty$ if $A_1 = B_1 = 0$ and then $e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant}$.

Case (ii) : When the roots of the equation (33) are real but equal, each of the roots is $\frac{r_1 x_1}{2k}$.

The general solution of (32) is therefore,

$$\lambda_1(t)e^{\delta t} = (A_2 + B_2 t)e^{\left(\frac{\eta x_1}{2k} + \delta\right)t} + \frac{M_1}{N_1},$$

where A_2 and B_2 are arbitrary constants.

In this case also, the shadow price $\lambda_1 e^{\delta t}$ remains bounded as $t \rightarrow \infty$ if $A_2 = B_2 = 0$ and $e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant}$.

Case (iii) : When m_1 and m_2 are complex conjugates with positive real parts, let $m_1 = \alpha_1 + i\beta_1$, $m_2 = \alpha_1 - i\beta_1$ where $\alpha_1 > 0$.

The solution of (32) then becomes

$$\lambda_1(t)e^{\delta t} = A_2 e^{(\alpha_1 + \delta)t} \cos(\beta_1 t + \varepsilon) + \frac{M_1}{N_1} \text{ where } A_2 \text{ and } \varepsilon \text{ are arbitrary constants.}$$

As $t \rightarrow \infty$ the first term becomes unbounded in an oscillatory manner. Hence the shadow price $e^{\delta t} \lambda_1(t)$ remains bounded as $t \rightarrow \infty$ iff $A_2 = 0$ so that we have

$$e^{\delta t} \lambda_1(t) = \frac{M_1}{N_1} = \text{constant.}$$

In a similar manner, we can show that, $\lambda_2(t)e^{\delta t} = \frac{M_2}{N_1} = \text{constant}$

where $M_2 = \delta p_2 q_2 E - \alpha x_1 p_1 q_1 E + \frac{r_1 x_1 p_2 q_2 E}{k}$.

Thus the shadow prices $e^{\delta t} \lambda_i(t)$ ($i = 1, 2$) remain constant over time in optimal equilibrium when they satisfy the transversibility condition at infinity^{14, 15} i.e., they remain bounded as $t \rightarrow \infty$. Now the last condition that the Hamiltonian H must be a maximum for an admissible control E leads to the condition

$$\begin{aligned} \frac{\partial H}{\partial E} &= e^{-\delta t} (p_1 q_1 x_1 + p_2 q_2 x_2 - c) - \lambda_1 q_1 x_1 - \lambda_2 q_2 x_2 = 0 \\ \Rightarrow \lambda_1 q_1 x_1 + \lambda_2 q_2 x_2 &= e^{-\delta t} \frac{\partial \pi}{\partial E}. \end{aligned} \quad (34)$$

This shows that the total user cost of harvest per unit effort must equal the discounted value of the future price at the optimal equilibrium level.

Equation (34) can also be written as

$$\begin{aligned} q_1 x_1 \left(p_1 - \frac{M_1}{N_1} \right) + q_2 x_2 \left(p_2 - \frac{M_2}{N_1} \right) &= c \\ \text{or, } q_1 x_1 \left(p_1 - \frac{\delta p_1 q_1 + \frac{r_2 x_2 p_2 q_2}{k}}{\delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 x_1 x_2 \alpha}{k}} E \right) + q_2 x_2 \left(p_2 - \frac{\delta p_2 q_2 - p_1 q_1 x_1 \alpha + \frac{r_1 x_1 p_2 q_2}{k}}{\delta^2 + \frac{r_1 x_1 \delta}{k} + \frac{r_2 x_1 x_2 \alpha}{k}} E \right) &= \end{aligned} \quad (35)$$

Eliminating E from (28) and (29), we get,

$$q_2 \left(r_1 - \frac{r_1 x_1}{k} - x_2 \alpha \right) = q_1 \left(\frac{r_2 x_1}{k} - \beta \right). \quad (36)$$

Equation (35) and (36) together determine the optimal equilibrium populations $x_1 = x_{18}$ and $x_2 = x_{28}$.

6. Numerical Example

Let us take the parameters of the system as

$$r_1 = 0.71, r_2 = 1.8, k = 600, \alpha = 0.0009, \beta = 1, c = 100, p_1 = 250, p_2 = 500,$$

$$\delta = 0.15, q_1 = 0.0006, q_2 = 0.0007, E = 20 \text{ in appropriate units.}$$

For the given parametric values, we find that the biological equilibrium occurs at the point (338, 331) and $\bar{E} \approx 306.26$, $E_{\max} \approx 360.18$.

Thus $0 < E (= 20) < \min(\bar{E}, E_{\max})$.

Therefore, criterion (b) determines that the non-trivial equilibrium point is a stable focus.

For the parametric values prescribed above, it is seen that the criteria (A) and (C) are satisfied implying that $x_{1\infty} > 0$ and $x_{2\infty} > 0$. Computations using (19) and (20) actually yield $x_{1\infty} \approx 389$ and $x_{2\infty} \approx 119$. It is interesting to note that the bionomic equilibrium for the prey species is established at a level higher than its biological equilibrium. On the other hand, the bionomic equilibrium for the predator occurs at a level which is much lower than its biological equilibrium. The optimal equilibrium solutions for the same numerical example obtained by solving (35) and (36) are $x_{1\delta} = 385$ and $x_{2\delta} = 134$. Thus the optimal equilibrium solution lies between the biological equilibrium and bionomic equilibrium.

For different initial values of $x_1(t)$, Fig. 3 depicts the time-course display for the prey density $x_1(t)$. The population density $x_1(t)$ is seen to undergo an oscillatory behaviour for smaller values of time t , whatever be the initial values $x_1(0)$. As t gets large, the population stabilizes at the biological equilibrium level.

Fig. 4 shows the time-course display for the predator density $x_2(t)$ for different initial values $x_2(0)$. Here also $x_2(t)$ exhibits an oscillatory behaviour for small times. Ultimately, it stabilizes to its biological equilibrium level.

The phase-plane trajectories of the dynamical system (2) are shown in Fig. 5. Clearly the biological equilibrium point P is a stable focus.

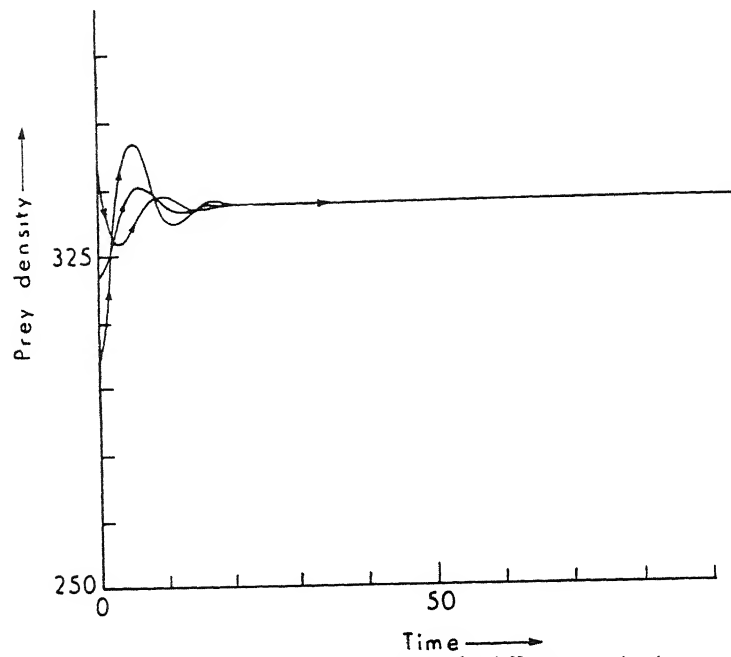


Fig 3—Time paths of the prey density for different initial values.

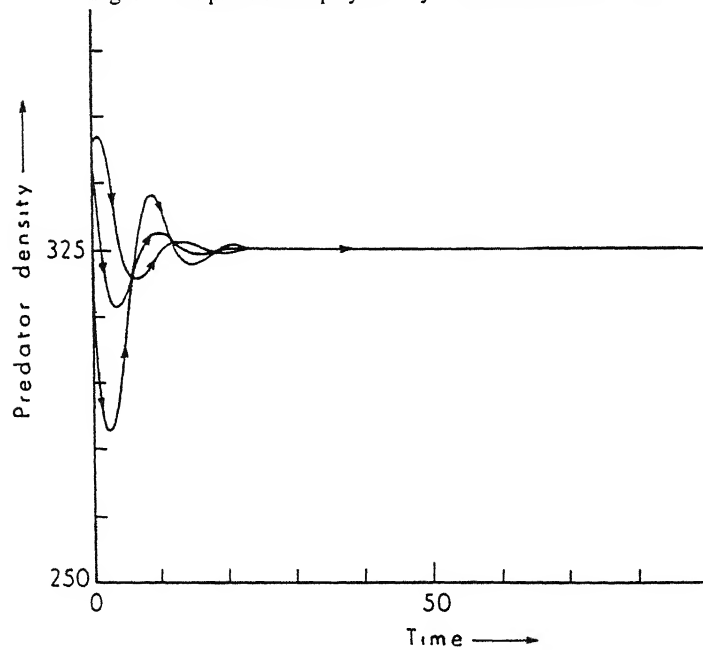


Fig 4—Time-paths of the predator density for different initial values

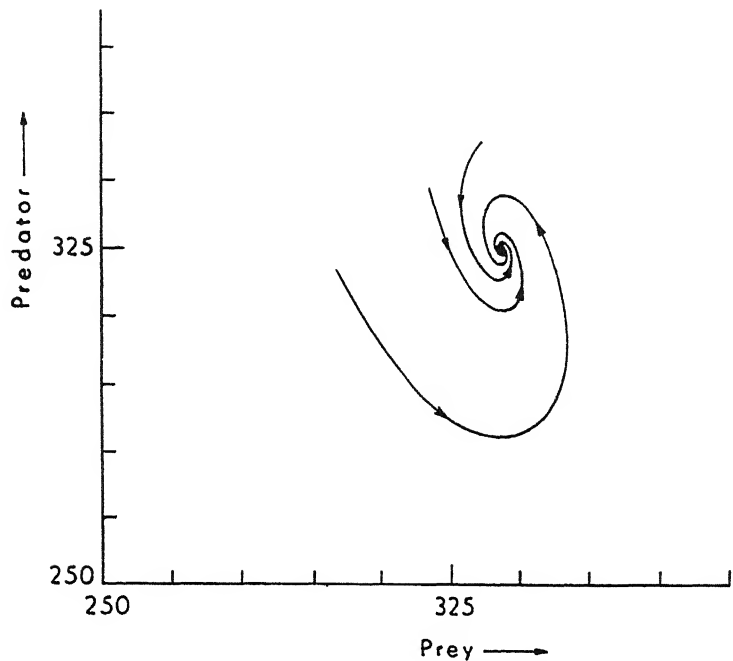


Fig 5–Phase plane trajectories of the system represented by equations (2)

7. Sensitivity Analysis

Using the above numerical example, the sensitivity analysis is performed to study the effects of changes of parameter values on the optimal solution.

Table 1– Effects of changes in the parameter values on optimal prey population and predator population

Parameters	% change in parameters	% change in x_{16}	% change in x_{25}
r_1	+30	5.33	-6.87
	+20	3.67	-4.72
	-20	-4.22	5.38
	-30	-6.58	8.36
r_2	+30	-18.67	23.63
	+20	-13.28	16.83
	-20	18.11	-23.25
	-30	29.90	-38.60

Table 2 Contd.

Table 2 Contd

k	+30	34.82	-44.59
	+20	22.92	-29.27
	-20	-21.84	27.71
	-30	-32.39	41.05
α	+30	-2.67	1.60
	+20	-1.76	0.98
	-20	1.70	-0.57
	-30	2.53	-0.65
c	+30	-6.30	69.49
	+20	-4.06	48.88
	-20	4.15	-49.95
	-30	6.32	-75.98
p_1	+30	3.71	-44.59
	+20	2.43	-29.27
	-20	-2.30	27.71
	-30	-3.41	41.06
p_2	+30	1.96	-23.55
	+20	1.42	-17.09
	-20	-2.21	26.60
	-30	-3.86	46.42
δ	+30	0.08	-0.97
	+20	0.05	-0.66
	-20	-0.06	0.70
	-30	-0.09	1.06
q_1	+30	0.23	-36.70
	+20	0.16	-24.36
	-20	-0.18	24.09
	-30	-0.28	36.05

Table 2 Contd

Table 2 Contd

q_2	+30	5.08	-25.83
	+20	3.50	-18.76
	-20	-4.02	28.88
	-30	-6.27	49.88
E	+30	-0.28	3.41
	+20	-0.19	2.27
	-20	0.19	-2.24
	-30	0.28	-3.35
β	+30	19.88	-25.40
	+20	13.25	-16.90
	-20	-13.25	16.82
	-30	-19.87	25.21

From the sensitivity analysis in Table – 1, the following points are observed.

- (1) both x_{18} and x_{28} are slightly sensitive to changes in the parameter r_1 , the biotic-potential of the prey. x_{18} increases while x_{28} decreases with increase in r_1 .
- (2) Both x_{18} and x_{28} are moderately sensitive and x_{28} is more sensitive than x_{18} to changes in r_2 , the biotic-potential of the predator. Also x_{18} decreases while x_{28} increases with the increase of r_2 .
- (3) Both x_{18} and x_{28} are quite sensitive and x_{28} is more sensitive than x_{18} to changes in k , carrying capacity of the prey. As k increases, x_{18} increases but x_{28} decreases.
- (4) Both x_{18} and x_{28} are insensitive to changes in α , the predation coefficient.
- (5) x_{18} has very low sensitivity while x_{28} possess very high sensitivity to changes in c , the cost per unit effort. As c increases, x_{18} decreases slowly, but x_{28} increases rapidly.

- (6) x_{18} is slightly sensitive while x_{28} is highly sensitive to changes in p_1 , the price per unit biomass of the prey. As p_1 increases, x_{18} increases slowly, but x_{28} decreases rapidly.
- (7) x_{18} is almost insensitive while x_{28} is quite sensitive to changes in p_2 , the price per unit biomass of the predator. x_{18} increases slightly but x_{28} decreases considerably as p_2 increases.
- (8) x_{18} and x_{28} are almost insensitive to changes in δ , the discount rate.
- (9) x_{18} is almost insensitive while x_{28} is considerably sensitive to changes in q_1 , the catchability coefficient of the prey. As q_1 increases x_{28} decreases and vice-versa.
- (10) x_{18} has low sensitivity and x_{28} has high sensitivity to changes in q_2 , the catchability coefficient of the predator. x_{18} undergoes slow increase and x_{28} undergoes rapid decrease as q_2 increases.
- (11) x_{18} is almost insensitive and x_{28} is slightly sensitive to changes in E , the level of harvesting effort. It should, however, be remembered that, this result holds for admissible values of E as per conditions (a) and (b).
- (12) Both x_{18} and x_{28} are quite sensitive to changes in β , the percapita death rate of the predator. x_{18} increases and x_{28} decreases with the increase of β .

8. Discussion

The present model is suitable for a fishery having a prey-predator community in which the prey density is high and that of the predators is low. An appropriate example might be a krill-whale fishery. For the numerical example taken here, we have determined three equilibria; biological equilibrium $P_1(338,331)$, bionomic equilibrium $P_2(389,119)$ and optimal equilibrium $P_3(385,134)$. P_1 is the most conservative of these three solutions. However, the economists may dislike it because it takes no economic factors into consideration. Although P_2 is based on economic considerations, its acceptability also is questionable because the fishery is, in this case, run on the no-profit-no-loss basis. P_3 seems to be the best choice for the fishery manager.

As far as the dynamical behaviour of the system is concerned, the existence of positive steady states for both the species depends primarily on their BTP's. These BTP's, on the other hand, depends on what types of fishing gear are being used, technical efficiency of the fishing gear is reflected in the catchability coefficients q_1 and q_2 . Thus the choice of the fishing gear is crucial for the survival of the species. The BTP's in turn, define upper and lower limits of the level of fishing effort E . These limits of E determine the behaviour of the steady state. Non-existence of any limit cycle of the system implies that the system does not undergo periodic oscillations. As we have seen in the case of local stability of the system, there are strict eigen-value inequalities: either (i) $\lambda_1 < 0$, $\lambda_2 < 0$ or (ii) λ_1, λ_2 are complex and $\text{Re } \lambda_i < 0$ ($i = 1, 2$). These strict eigenvalue inequalities are preserved by small changes in the elements of the eigen matrix. Thus the stable node in case (i) and the stable focus in case (ii) are stable relative to small perturbations of the parameters r_1, r_2, α, β and k . Hence the dynamical system (2) represents a reasonable model of a biological system. The global asymptotic stability of the steady state implies that the behaviour of the solution trajectories does not change drastically if the model is subject to small perturbations.

As we have already seen in Figs. 2(b) and 2(d), practically no bionomic equilibrium exists because (17) and (18) intersect at a point with $x_{1\infty} < 0$. In such a case, as Clark² (p. 305) says, the two lines do not intersect, and bionomic equilibrium occurs at the point $(0, x_{2\infty})$. This view is untenable because the bionomic equilibrium state is defined as the point of the state plane in which both the conditions (17) and (18) are satisfied. It is also seen from (19) that $x_{1\infty} \rightarrow 0$ and $x_{2\infty} \rightarrow \frac{q_1\beta + q_2r_1}{q_2\alpha}$ (a finite quantity) only when p_2 is finite and $p_1 \rightarrow \infty$. This cannot be a practical situation. The same observation holds for the situations depicted in Figs. 2(c) and 2(e) also. Thus there cannot be any bionomic equilibrium with one species extinct as concluded by Clark². Positive bionomic equilibria of both the species exist when p_1 and p_2 are both finite and other conditions, as discussed in section 4, are satisfied.

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Creep transition in torsion of a non-homogeneous cylinder

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Abstract

Creep transition in a circular non-homogeneous cylinder, subjected to torsion has been studied by transition approach. Non-homogeneity in the material is considered due to radial variation of modulus of rigidity. Stresses for steady state creep have been derived and discussed numerically. Effects of the non-homogeneity appear to be prominent and the same shear stress distribution has been found for different combinations of the non-homogeneity parameter k and the measure n . Moreover, non-homogeneity of a certain type having more value at the outer radius than at the centre of the cylinder may be beneficial from a design point of view.

(Keywords : creep/torsion/generalised measure)

Introduction

The 327 page paper presented to the French Academy by St. Venant¹, about one and half century ago remains the most outstanding work on the torsion of cylinders of arbitrary cross-section, that, is circular, elliptical, rectangular, equilateral, triangular etc., and the topic entered many texts²⁻⁵. Lee⁶ considered the torsion of an elastic perfectly plastic cylindrical bar and showed that the curvature of the shearing stress lines in the plastic zone has an upper bound proportional to the twisting angle, while Cho and Findley⁷ studied creep and plastic strains under side steps to tension and torsion for 304 stainless steel at 593°C. An analysis for the creep deformation of a thin-walled cylinder subjected to axial force, bending and twisting moment, was carried out by Lau *et. al.*⁸ under the assumptions of Prandtl-Nadai creep law and incompressibility of the material.

The problem of torsion of a semi-infinite isotropic, homogeneous, elastic solid when a circular cylinder welded to its plane boundary and is forced to rotate about its axis was first discussed by Reissner and Sagoci⁹. Erguven¹⁰ worked on the Reissner-Sagoci problem for a transversely isotropic, non-homogeneous elastic solid by varying the modulus of rigidity as a power of the radial co-ordinate and a note on the twisting of a non-homogeneous sphere has been furnished by Chaudhuri and Datta¹¹ on the

basis of classical theory of elasticity. In an investigation Cowin¹² observed that for a certain class of elastic cylinders with shape intrinsic orthotropy, the solution to the torsion problem is the same as the solution to the torsion problem for the isotropic cylinder of the same shape if the isotropic shear modulus were replaced by the orthotropic cylinders by considering the finite strains incompressibility of the material and Norton's law of creep.

In this paper an attempt has been made to study creep transition in torsion of a non homogeneous cylinder with the help of transition approach. Transition theory developed by Seth^{14,15} does not require any adhoc assumptions like incompressibility of the material or creep strain law, and solves a more general problem from which cases pertaining to such assumptions can be worked out¹⁶⁻²³. It utilises the concept of generalised strain measure and asymptotic transition through the critical points of the differential system defining the deformed field. For uni-axial case, Seth¹⁴ has defined the generalised strain measure as

$$e = (1/n \{1 - \{l_0/l\}^n\})^m \quad (1)$$

where n is the measure, m the irreversibility index, l_0 and l are the initial and strained length of the rod respectively.

Here, a secondary stage of creep, i.e., $m=1$ has been considered and non-homogeneity in the material is taken due to radial variation of modulus of rigidity

$$\mu = \mu_0 r^{-k} \quad (2)$$

where μ_0 and k are real constants.

Governing Equations

Considering a long circular cylinder of radius a subjected to finite twist. Let r, θ, z refer to the radial, tangential and axial directions of the cylinder and z -axis is coincident with its long axis. The components of displacement are given by^{15,19}

$$u = r(1-\beta), v = \alpha r z, w = d_1 z, \quad (3)$$

where d_1 is a constant, α is the angle of twist per unit length and β is a function of

$$r = (x^2 + y^2)^{1/2} \text{ only.}$$

The generalised components of strain from eqn. (1) are^{19,20}

$$\left. \begin{aligned} e_{rr} &= 1/n [1 - (r\beta' + \beta)^n], \quad e_{\theta\theta} = 1/n [1 - \beta^n], \\ e_{zz} &= 1/n [d_2 - (\alpha r\beta)^n], \quad e_{\theta z} = 1/n (\alpha r)^{n/2} \beta^n, \\ e_{r\theta} &= e_{zr} = 0, \end{aligned} \right\} \quad (4)$$

where

$$d_2 = 1 - (1 - d_1)^n \text{ and } \beta' = d\beta/dr$$

Stress-strain relations are

$$\tau_{ij} = \lambda \delta_{ij} e_{ii} + 2\mu e_{ij}, \quad (i, j = 1, 2, 3) \quad (5)$$

where τ_{ij} and e_{ij} are the stress and strain tensors respectively, λ and μ are Lamé's constants and δ_{ij} is Kronecker's delta.

Substituting eqn. (4) into eq. (5), one gets

$$\left. \begin{aligned} \tau_{rr} &= \lambda S_1 + 2\mu [1 - (r\beta' + \beta)^n] / n, \quad \tau_{\theta\theta} = \lambda S_1 + 2\mu [1 - \beta^n] / n, \\ \tau_{zz} &= \lambda S_1 + 2\mu [d_2 - (\alpha r\beta)^n] / n, \quad \tau_{\theta z} = 2\mu \beta^n (\alpha r)^{n/2} / n, \\ \tau_{r\theta} &= \tau_{\theta z} = 0, \end{aligned} \right\} \quad (6)$$

where $S_1 = [2 + d_2 - \beta^n - (r\beta' + \beta)^n - (\alpha r\beta)^n] / n$.

Equation of equilibrium to be satisfied is²⁰

$$\partial \tau_{rr} / \partial r + (\tau_{rr} - \tau_{\theta\theta}) / r = 0 \quad (7)$$

Substituting from eqn. (6) into eqn. (7), one gets a non-linear differential eqn. in β as

$$\begin{aligned}
 (\lambda+2\mu)\beta P(P+1)^{n-1}dP/d\beta &= 2\mu[1-(P+1)^n]/n + 2\mu'r[\beta^n-(P+1)^n]/n \\
 &- \lambda(\alpha r)^n - P[\lambda(1+\alpha^n r^n) + (\lambda+2\mu)(P+1)^n],
 \end{aligned} \quad (8)$$

where $r\beta' = \beta P$ and $\mu' = d\mu/dr$

Transition points of β in eq. (8) are

$$P \rightarrow 0, -1, \pm \infty.$$

Torque applied is

$$M = 2\pi \int_0^a r^2 \tau_{\theta z} dr \quad (9)$$

Statement and Mathematical Model of the Problem

Following the transition approach, we analyse the problem of creep transition in torsion of a cylinder made of the material having variable modulus of rigidity along the radius, and governed by eqn. (2), (6) to (9). It is of interest to investigate the actual variation of the creep stresses on the assumption that the radial stress vanishes on the free surface and no longitudinal force acts on transverse sections of the cylinders i.e.

$$\tau_{rr} = 0, \text{ at } r = a \quad (10)$$

$$\text{and } \int_0^a 2\pi r \tau_{zz} dr = 0 \quad (11)$$

Solution of the Problem

It has been shown by several workers¹⁹⁻²³ that the asymptotic transition through the principal stress difference gives creep stresses at the transition point $P \rightarrow -1$. Therefore, we take the transition function R_1 as^{19, 21}.

$$R_1 = \tau_{rr} - \tau_{\theta\theta} = 2\mu\beta^n[1-(P+1)^n]/n \quad (12)$$

Taking logarithmic differentiation of eqn. (12), with respect of r , we get

$$d/dr(\ln R_1) = \mu'/\mu + nP \{ 1 - [\beta(P+1)^{n-1}/1 - (P+1)^n] dP/d\beta \} / r \quad (13)$$

Substituting the value of $dP/d\beta$ from eq. (8) in eq. (13) and taking the asymptotic value as

$P \rightarrow -1$, after integration one obtains

$$R_1 = \tau_{rr} - \tau_{\theta\theta} = A_1 \mu r^{-2n} \exp f(r), \quad (14)$$

where A_1 is a constant of integration and

$$f(r) = \int [(n-1)c/r - (c'/1-c)\beta^{-n}] dr, c' = dc/dr, c = 2\mu/\lambda + 2\mu$$

Substituting eqn. (14) into eqn. (7) and integrating

$$\tau_{rr} = A_2 - A_1 I_1(r), \quad (15)$$

$$\text{and } \tau_{\theta\theta} = \tau_{rr} - A_1 \mu r^{-2n} \exp f(r), \quad (16)$$

where A_2 is a constant of integration and

$$I_1(r) = \int \mu r^{-2n-1} \exp f(r) dr.$$

The asymptotic value of β , obtained from solving eqn. (12) and (14) as

$$\beta^n = (A_1/2) n r^{-2n} \exp f(r) \quad (17)$$

In view of eqs. (6) and (17), other stresses in the cylinder are

$$\tau_{zz} = \{ (1-c)/2-c \} [\tau_{rr} + \tau_{\theta\theta}] + \{ 2d_2/n - A_1 S_3 \} S_2/r, \quad (18)$$

$$\text{and } \tau_{\theta z} = A_1 S_4, \quad (19)$$

where $S_2 = \{ (3-2c)/2-c \} \mu r$, $S_3 = \alpha^n r^{-n} \exp f(r)$,

$$S_4 = \mu \alpha^{n/2} r^{-3n/2} \exp f(r)$$

Applying bounding conditions (10) and (11) to eqn. (15) and (18), we obtain

$$A_2 = A_1 I_1(a), A_1 = -2d_2 I_2 / n I_3, \quad (20)$$

where

$$I_2 = \int_0^a S_2 dr, I_3 = \int_0^a \{ [I_1(a) - I_1(r)] r^2 c' / (2-c)^2 - S_2 S_3 \} dr$$

The twisting couple in the cylinder is given by

$$M = 2\pi A_1 \int_0^a r^2 S_4 dr \quad (21)$$

Eqn. (15), (16), (18) to (21) provide transitional stresses for stationary state of creep for a cylinder made of the material having variable modulus of rigidity, subjected to torsion.

For a cylinder having non-homogeneity in accordance with eqn. (2), the transitional creep stresses obtained by substituting eqn. (2) into eqn. (15), (16), (18) to (21) as

$$\left. \begin{aligned} \tau_{rr} &= A_3 [I_4(a) - I_4(r)], \\ \tau_{\theta\theta} &= A_3 [I_4(a) - I_4(r) - S_5], \\ \tau_{zz} &= A_3 S_6 [2I_4(a) - 2I_4(r) - S_5] + S_7 (2\mu_0 d_2 / n - A_3 \alpha^n S_8), \\ \tau_{\theta z} &= A_3 \alpha^{n/2} S_9, \quad M = 2\pi A_3 \alpha^{n/2} I_7, \end{aligned} \right\} \quad (22)$$

where

$$\begin{aligned} A_3 &= 2\mu_0 d_2 [a^{2-k}/2 - k + I_6] / n I_5, I_4(r) = \int_0^a S_5 / r dr, I_7 = \int_0^a r^2 S_9 dr, \\ I_6 &= \int_0^a [r / (2r^k + t)] dr, I_5 = \int_0^a \{ kt S_{10} [I_4(a) - I_4(r)] + \alpha^n S_{11} \} dr, \end{aligned}$$

$$\begin{aligned}
 S_5 &= r^{t_1} \exp f_1, S_6 = r^k / 2r^k + t, S_7 = (3 + tr^{-k}) / 2r^k + t, S_8 = r^{-n} \exp f_1, \\
 S_9 &= r^{t_2} \exp f_1, S_{10} = r^{k+1} / (2r^k + t)^2, S_{11} = S_7 r^{1-n} \exp f_1, t = 2\mu_0 / \lambda \\
 t_1 &= -k - 2n, t_2 = -k - 3n/2, f_1 = (n-1)t[dr/r(r^k + t) + kt/d_0^n][r^{n-1}/r^k + t]dr, \\
 \beta &\rightarrow d_0/r, d_0 \text{ being a constant.}
 \end{aligned}$$

For an incompressible material, that is, $\lambda \rightarrow \infty^{23, 24}$, eqn. (22) gives

$$\left. \begin{aligned}
 \tau_{rr} &= A_4(a^{t_1} - r^{t_1})/t_1, \tau_{\theta\theta} = A_4[a^{t_1} - [1 + t_1]r^{t_1}]/t_1, \\
 \tau_{zz} &= A_4[a^{t_1} - (1 + t_1/2)r^{t_1}]/t_1 + (E_0 d_2/n - 3A_4 \alpha^n r^{-n}/2)r^{-k}, \\
 \tau_{\theta z} &= A_4 \alpha^{n/2} r^{t_2}, M = 2\pi A_4 \alpha^{n/2} a^{t_3}/t_3,
 \end{aligned} \right\} (23)$$

where $\mu_0 \rightarrow E_0/3$, E_0 is the constant value of Young's modulus,

$$t_3 = 3 + t_2, A_4 = 2(2 - k - n)E_0 d_2 a^n / 3(2 - k)n \alpha^n.$$

For homogeneous case, that is, $k = 0$, c_0 is a constant and eqn. (14) reduces to

$$\tau_{rr} - \tau_{\theta\theta} = A_1 r^{t_4}, \quad (24)$$

where $t_4 = (n-1)c_0 - 2n$.

Consequently, the transitional stresses for steady state creep become

$$\left. \begin{aligned}
 \tau_{rr} &= A_1(a^{t_4} - r^{t_4})/t_4, \tau_{\theta\theta} = A_1[a^{t_4} - (1 + t_4)r^{t_4}]/t_4, \\
 \tau_{zz} &= A_1(1 - c_0)[2a^{t_4} - (2 + t_4)r^{t_4}]/t_4(2 - c_0) + \{3 - 2c_0\}[2\mu_0 d_2/n - A_1 \alpha^n r^{t_5}]/2 - c_0, \\
 \tau_{\theta z} &= A_1 \alpha^{n/2} r^{t_6}, M = 2\pi A_1 \alpha^{n/2} a^{t_7} / t_7,
 \end{aligned} \right\} (25)$$

where $t_5 = (n-1)c_0 - n, t_6 = (n-1)c_0 - 3n/2, t_7 = 3 + t_6$,

$$A_1 = (2 + t_5)\mu_0 d_2 / n \alpha^n a^{t_5}.$$

Numerical Discussion

In the specific case, calculations have been made for the shear stress ratio $\tau = \tau_{\theta z} / M_1$, where $M_1 = M/2 \pi a^3$, for different combinations of k and n , using eqn. (23). Fig. 1 shows variation of the creep shear stress ratio, τ with radii ratio, $R = r/a$ of the non-homogeneous incompressible cylinder under torsion. It can be observed that the shear stress is maximum at the outer radius of the cylinder for the non-homogeneity $k < 0$ with smaller values of the measure n , $0 < n \leq 2/3$. For $k \geq 0$, the shear stress is found to be maximum at the centre of the cylinder and its value increases abruptly at the centre with increasing k and n . However, the same shear stress distribution can be obtained for various values of k and n , and the stress remains constant through the

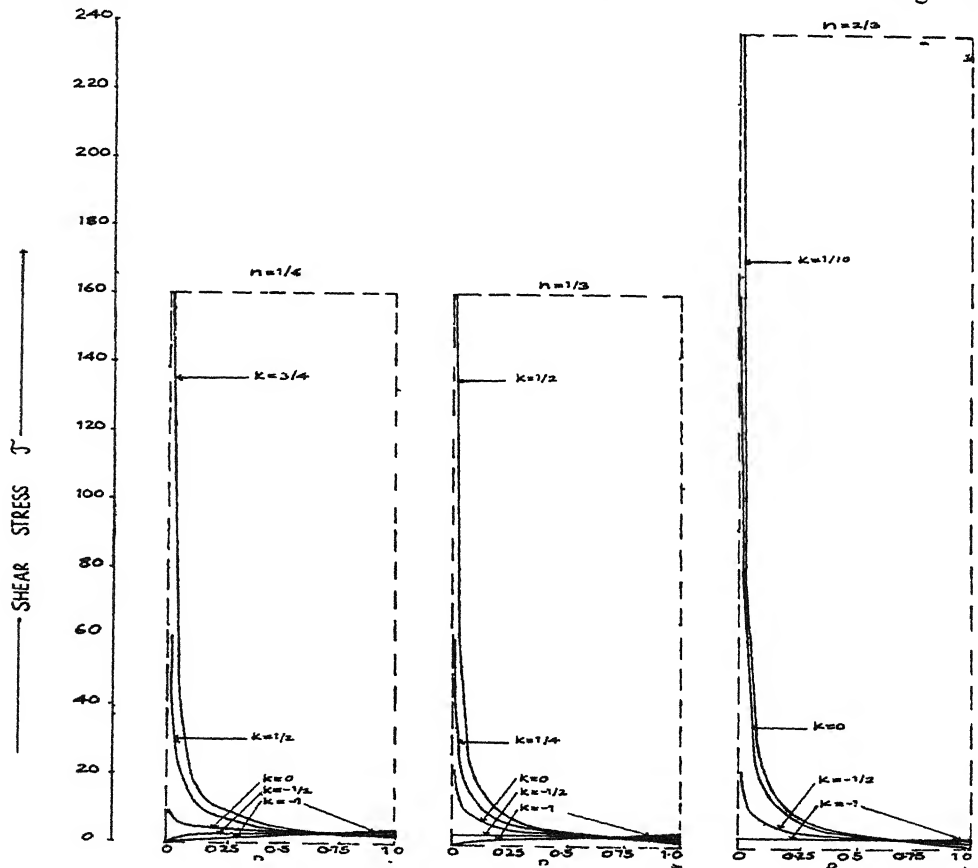


Fig. 1—Variation of shear stress in a non-homogeneous ($\mu = \mu_0 r^{-k}$) cylinder under torsion

cylinder for the combinations $n = 1/3$, $k = -1/2$ and $n = 2/3$, $k = -1$. This may provide a choice to the designer in selecting an appropriate material for the manufacture of cylindrical components.

Numerical calculations reveal that the shear stress ratio reduces to zero for the homogeneous material ($k=0$) with $n=2$, as the torque M required in this case, theoretically becomes infinitely large, and the stress appears to be negative for $k>0$ and $n \geq 2$. More realistic knowledge regarding the effects of non-homogeneity on the creep stresses of cylinders of various materials, subjected to torsion can be obtained from the numerical discussion of eqn. (22). For example, taking Poisson's ratio $\nu_0 = 1/3$, the value of t from eqn. (22) comes out to be unity and integrals may be evaluated by Simpson's rule for suitable values of k , n etc.

Thus, the effects of non-homogeneity of the assumed form on the torsion of cylinder in the theory of creep are prominent. The presence of non-homogeneity $k<0$, reduces magnitude of the shear stress significantly and may be beneficial from a design point of view, while for $k>0$, the stress increases promptly at the centre of the incompressible cylinder and may not be useful with higher values of k and n .

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Eigen value approach to a micropolar viscoelastic medium

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Abstract

The dynamic problem in micropolar viscoelastic medium has been investigated by employing eigenvalue approach after applying Laplace and Hankel transformations. An example of infinite space with concentrated force at the origin has been presented to illustrate the application of the approach. The integral transforms have been inverted by using a numerical technique to obtain the radial displacement, normal displacement, normal force stress, shear stress, couple stress and microrotation in the physical domain. The results for these quantities are given and illustrated graphically.

(Keywords) micropolar viscoelastic medium/eigen value/Hankel and Laplace transformation)

Introduction

Modern engineering structures are often made up of materials possessing an internal structure. Polycrystalline materials, materials with fibrous or coarse grain structures come in this category. Classical elasticity is inadequate to represent the behaviour of such materials. The analysis of such materials require incorporating the theory of oriented media. For this reason, micropolar theories were developed by Eringen¹⁻³ for elastic solid, fluids and further for non-local polar fields and are now universally accepted. A micropolar continuum is a collection of interconnected particles in form of small rigid bodies undergoing both translational and rotational motions. Different authors⁴⁻¹³ discussed different type of problems in micropolar elastic medium.

Eringen¹⁴ extended the theory of micropolar elasticity to obtain linear constitutive theory for micropolar material possessing internal friction. A problem on micropolar

viscoelastic waves has been discussed by McCarthy and Eringen¹⁵. They discussed the propagation conditions and growth equations governing the propagation of waves in micropolar viscoelastic medium. Cicco and Nappa¹⁶ discussed a problem of Saint Venant's principles for micropolar viscoelastic bodies. Kumar *et al.*¹⁷ studied Lamb's plane problem in a micropolar viscoelastic half-space with stretch. Recently, Kumar¹⁸ discussed wave propagation in micropolar viscoelastic generalized thermoelastic solid. Most of the problems studied so far, in micropolar viscoelastic, involve the use of potential functions. However, the use of the eigen value approach has the advantage of finding the solution of eqns in the coupled form directly, in the matrix notations, whereas the potential function approach requires decoupling of eqns. Yet, much work has not been done in micropolar viscoelastic solid using the eigen value approach. Mahalanabis and Manna¹⁹ applied eigen-value approach of linear micropolar elasticity by arranging basic eqns of linear micropolar viscoelastic in the form of matrix differential eqn. Recently, Mahalanabis and Manna²⁰ discussed the problem of linear micropolar thermoelasticity by using eigen value approach.

In this paper, we consider a two dimensional axisymmetric problem in a homogeneous isotropic micropolar viscoelastic medium. The solutions were obtained by using eigen value approach after employing integral transformations technique. The integral transforms were inverted using a numerical approach.

Basic Equations

Following Eringen¹⁴ the constitutive relations and the field eqns in micropolar viscoelastic solid without body forces and body couples can be written as

$$t_{ij} = \lambda_l u_{k,k} \delta_{ij} + \mu_l (u_{i,j} + u_{j,i}) + K_l (u_{j,i} - \epsilon_{ijk} \phi_k), \quad (1)$$

$$m_{ij} = \alpha_l \phi_{k,k} \delta_{ij} + \beta_l \phi_{i,j} + \gamma_l \phi_{j,i}, \quad (2)$$

$$(\lambda_l + 2\mu_l + K_l) \Delta \Delta \vec{u} - (\mu_l + K_l) \Delta \times \Delta \times \vec{u} + K_l \Delta \times \vec{\phi} = \rho \frac{\partial^2 \vec{u}}{\partial t^2} \quad (3)$$

$$(\alpha_l + \beta_l + \gamma_l) \Delta \nabla \vec{\phi} + K_l \Delta \times \vec{u} - 2K_l \vec{\phi} = \rho j \frac{\partial^2 \vec{\phi}}{\partial t^2} \quad (4)$$

where,

$$\lambda_1 = \lambda + \lambda_\nu \frac{\partial}{\partial t}, \quad \mu_1 = \mu + \mu_\nu \frac{\partial}{\partial t}, \quad K_1 = K + K_\nu \frac{\partial}{\partial t} \quad (5)$$

$$\alpha_1 = \alpha + \alpha_\nu \frac{\partial}{\partial t}, \quad \beta_1 = \beta + \beta_\nu \frac{\partial}{\partial t}, \quad \gamma_1 = \gamma + \gamma_\nu \frac{\partial}{\partial t} \quad (6)$$

where, $\lambda, \mu, K, \alpha, \beta, \gamma, \lambda_\nu, \mu_\nu, K_\nu, \alpha_\nu, \beta_\nu, \gamma_\nu$ are material constants, ρ is the density, j is the micro inertia, \vec{u} is the displacement vector, $\vec{\phi}$ is the microrotation vector, t_{ij} is the force stress tensor, m_{ij} is the couple stress tensor. The necessary and sufficient conditions for the internal energy to be non-negative, as given by Eringen¹⁴ are

$$\begin{aligned} 0 \leq 3\lambda + 2\mu + K, & \quad 0 \leq \mu, & \quad 0 \leq K \\ 0 \leq 3\alpha + 2\gamma & \quad -\gamma \leq \beta \leq \gamma, & \quad 0 \leq \gamma \end{aligned} \quad (7)$$

and

$$\begin{aligned} 0 \leq 3\lambda_\nu + 2\mu_\nu + K, & \quad 0 \leq \mu, & \quad 0 \leq K \\ 0 \leq 3\alpha_\nu + 2\gamma_\nu & \quad -\gamma_\nu \leq \beta_\nu \leq \gamma_\nu, & \quad 0 \leq \gamma_\nu \end{aligned} \quad (7)$$

Formulation and Solution

We consider a homogeneous, isotropic micropolar viscoelastic medium of infinite extent with cylindrical polar co-ordinate system (r, θ, z) . To analyze displacement and stresses at the interior of the medium due to concentrated load, the continuum is divided into two half-space defined by

$$\bullet \text{Half-space I: } |r| < \infty \quad -\infty < z \leq 0,$$

$$\bullet \text{Half-space II: } |r| < \infty \quad 0 \leq z < \infty.$$

As we are discussing an axi-symmetric problem so we take

$$\vec{u} = (u_r, 0, u_z), \quad \vec{\phi} = (0, \phi_\theta, 0) \quad (9)$$

We define dimensionless quantities as

$$\begin{aligned} r' &= \frac{r}{h}, \quad z' = \frac{z}{h}, & u'_r &= \frac{\rho h \omega^{*2} u_r}{\mu_1}, & u'_z &= \frac{\rho h \omega^{*2} u_z}{\mu_1}, \\ \phi'_\theta &= \frac{\rho h^2 \omega^{*2} u_r}{\mu_1} \phi_\theta, & t' &= \frac{\mu}{\rho h^2 \omega^*} t, & t'_z &= \frac{1}{K_1} t_z, \\ t'_z &= \frac{1}{K_1} t_z, & m'_{z\theta} &= \frac{1}{K_1} m_{z\theta}, & \omega^{*2} &= \frac{K_1}{\rho j} \end{aligned} \quad (10)$$

where h is a constant having dimension of length.

Due to axi symmetry about z -axis the quantities are independent of θ . With these considerations and using (9) and (10) in eqns. (3) and (4) we obtain : (on suppressing the primes).

$$\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \right] u_r + (1 - a^2) \frac{\partial^2 u_z}{\partial r \partial z} + a^2 \frac{\partial^2 u_r}{\partial z^2} - s_4^* \frac{\partial \phi_\theta}{\partial z} = \frac{1}{(s_1 + s_2)} \frac{\partial^2 u_r}{\partial t^2}, \quad (11)$$

$$\frac{\partial^2 u_z}{\partial z^2} + (1 - a^2) \left[\frac{\partial^2 u_r}{\partial r \partial z} + \frac{1}{r} \frac{\partial u_r}{\partial z} \right] + a^2 \left[\frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r} \frac{\partial u_z}{\partial r} \right] + s_4^* \frac{1}{r} \frac{\partial}{\partial r} (r \phi_\theta) = \frac{1}{(s_1 + s_2)} \frac{\partial^2 u_z}{\partial t^2}, \quad (12)$$

$$s_4 \left[\frac{\partial^2 \phi_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial \phi_\theta}{\partial r} + \frac{\partial^2 \phi_\theta}{\partial z^2} - \frac{\phi_\theta}{r^2} \right] - \frac{h^2 s_3 \phi_\theta}{j} + \frac{2h^2 s_3}{j} \left(\frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r} \right) = \frac{\partial^2 \phi_\theta}{\partial t^2} \quad (13)$$

where

$$s_1 = \frac{\rho h^2 (\lambda_I + \mu_I) \omega^2}{\mu_I^2}, \quad s_2 = \frac{\rho h^2 (\mu_I + K_I) \omega^2}{\mu_I^2}, \quad s_3 = \frac{\rho h^2 K_I \omega^2}{\mu_I^2},$$

$$s_4 = \frac{\gamma_I \rho h^2 \omega^2}{j \mu_I^2}, \quad a^2 = \frac{s_2}{s_1 + s_2}, \quad s_4^* = \frac{s_3}{s_1 + s_2}.$$

Applying Laplace transform w.r.t. time variable 't' defined by

$$\{\bar{u}_r(r, z, p), \bar{u}_z(r, z, p), \bar{\phi}_\theta(r, z, p) = \int_0^\infty \{u_r(r, z, t), u_z(r, z, t), \phi_\theta(r, z, t)\} e^{-pt} dt \quad (14)$$

and then Hankel transform w.r.t. space variable 'r' defined by

$$\{\tilde{u}_r(\xi, z, p), \tilde{\phi}_\theta(\xi, z, p)\} = \int_0^\infty \{u_r(r, z, p)(z, r, p), u_z(r, z, p), \bar{\phi}_\theta(r, z, p)\} r J_0(\xi r) dr, \quad (15)$$

$$\bar{u}_r(\xi, z, p) = \int_0^\infty \bar{u}_r(r, z, p) r J_1(\xi r) dr, \quad (16)$$

on eqns (11) – (13), we obtain

$$\tilde{u}_r'' = \frac{1}{a^2} \left[\xi^2 + \frac{p^2}{s_1 + s_2} \right] \bar{u}_r + \frac{(1-a^2)\xi}{a^2} \tilde{u}_z' + \frac{s_4^*}{a^2} \tilde{\Phi}_\theta, \quad (17)$$

$$\tilde{u}_z'' = \left[a^2 \xi^2 + \frac{p^2}{s_1 + s_2} \right] \bar{u}_z - (1-a^2) \xi \tilde{u}_r' - \xi s_4^* \tilde{\Phi}_\theta', \quad (18)$$

and

$$\tilde{\Phi}_\theta'' = -\frac{K_1 h^2}{\gamma_1} \tilde{u}_r' - \frac{K_1 h^2 \xi}{\gamma_1} \tilde{u}_z' + \left[\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right] \tilde{\Phi}_\theta, \quad (19)$$

The system of eqns. (17) – (19) can be written as

$$\frac{d}{dz} W(\xi, z, p) = A(\xi, p) W(\xi, z, p), \quad (20)$$

where,

$$W = \begin{bmatrix} U \\ U' \end{bmatrix}, \quad A = \begin{bmatrix} 0 & I \\ A_2 & A_1 \end{bmatrix}, \quad U = \begin{bmatrix} \tilde{u}_r \\ \tilde{u}_z \\ \tilde{\Phi}_\theta \end{bmatrix}$$

$$O = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad I = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$A_1 = \begin{bmatrix} 0 & \frac{(1-a^2)\xi}{a^2} & \frac{s_4^*}{a^2} \\ -(1-a^2)\xi & 0 & 0 \\ -\frac{K_1 h^2}{\gamma_1} & 0 & 0 \end{bmatrix}$$

$$A_1 = \begin{bmatrix} \frac{1}{a^2} \left(\xi^2 + \frac{p^2}{(s_1 + s_2)} \right) & 0 & 0 \\ 0 & a^2 \xi + \frac{p^2}{(s_1 + s_2)} & -s_4^* \xi \\ 0 & -\frac{K_1 \xi h^2}{\gamma_1} & \xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \end{bmatrix} \quad (21)$$

To solve eqn. (20), we take

$$W(\xi, z, p) = X(\xi, p) e^{qz} \quad (22)$$

so that

$$A(\xi, p) W(\xi, z, p) = q W(\xi, z, p) \quad (23)$$

which leads to eigen value problem. The characteristic eqn. corresponding to the matrix A is given by

$$\det [A - qI] = 0 \quad (24)$$

which on expansion provides us

$$q^6 - \lambda_1 q^4 + \lambda_2 q^2 - \lambda_3 = 0$$

where

$$\lambda_1 = \left(1 + \frac{1}{a^2} \right) \frac{p^2}{(s_1 + s_2)} + \left[3\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} - \frac{K_1 h^2 s_4^*}{\gamma_1 a^2} \right] \quad (26)$$

$$\lambda_2 = \left[\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right] \left[\frac{p^2}{(s_1 + s_2)} + \left(1 + \frac{1}{a^2} \right) 2\xi^2 \right]$$

$$-s_4^* \frac{K_1 h^2}{\gamma_1 a^2} \left[2\xi^2 + \frac{p^2}{(s_1 + s_2)} \right] + \frac{1}{a^2} \left[\xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[a^2 \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \quad (27)$$

and

$$\lambda_3 = \frac{1}{a^2} \left[\xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[a^2 \xi^2 + \frac{p^2}{(s_1 + s_2)} \right] \left[\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right] - \frac{1}{\gamma_1 a^2} \left[\xi^2 + \frac{p^2}{(s_1 + s_2)} \right] s_4^* K_1 h^2 \xi^2.$$

The roots of eqn. (25) are $\pm q_i, i = 1, 2, 3$.

The eigen value of the matrix A are the roots of eqn. (25). We assume that real part of q_i are positive. The vector $X(\xi, p)$ corresponding to the eigen values q_i can be determined by solving the homogeneous eqn.

$$[A - qI] X(\xi, p) = 0 \quad (29)$$

The set of eigen vectors $X_i(\xi, p), (i = 1, 2, 3, 4, 5, 6)$ may be obtained as

$$X_i(\xi, p) = \begin{bmatrix} X_{i1}(\xi, p) \\ X_{i2}(\xi, p) \end{bmatrix} \quad (30)$$

where,

$$X_{i1}(\xi, p) = \begin{bmatrix} a_i q_i \\ b_i \\ -\xi \end{bmatrix}, \quad X_{i2}(\xi, p) = \begin{bmatrix} a_i q_i^2 \\ -b_i q_i \\ \xi q_i \end{bmatrix}, \quad q = q_i, i = 1, 2, 3 \quad (31)$$

$$X_{j1}(\xi, p) = \begin{bmatrix} -a_i q_i \\ b_i \\ -\xi \end{bmatrix}, \quad X_{j2}(\xi, p) = \begin{bmatrix} a_i q_i^2 \\ -b_i q_i \\ \xi q_i \end{bmatrix}, \quad j=i+3, \quad q=-q_i, \quad i=1,2,3 \quad (32)$$

$$a_i = \left[\xi(a^2 - 1) \left\{ \left(\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) - q_i^2 \right\} - \frac{K_1 \xi h^2 s_4^*}{\gamma_1} \right] / \Delta \quad (33)$$

$$b_i = \left[\left(\xi^2 + \frac{p^2}{(s_1 + s_2)} \right) \left(\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) + a^2 q_i^2 \left\{ q_i^2 - \left(\xi^2 + \frac{2K_1 h^2}{\gamma_1} + \frac{p^2}{s_4} \right) \right. \right. \\ \left. \left. - \left(\xi^2 + \frac{p^2}{(s_1 + s_2)} \right) q_i^2 + \frac{K_1 s_4^* h^2 q_i^2}{\gamma_1} \right\} \right] / \Delta \quad (34)$$

$$\Delta = \frac{K_1 h^2}{\gamma_1} \left[q_i^2 - \left(\xi^2 + \frac{p^2}{(s_1 + s_2)} \right) \right] \quad (35)$$

The solution of eqn. (20) is given by

$$W(\xi, z, p) = \sum_{i=1}^3 [B_i X_i(\xi, p) \exp(q_i z) + B_{i+3} X_{i+3}(\xi, p) \exp(-q_i z)]$$

where, B_i ($i = 1, 2, 3, 4, 5, 6$) are arbitrary constants.

The eqn. (36) represents the solution of the general problem in the axisymmetric case of homogeneous isotropic, micropolar viscoelasticity by employing the eigen value approach and therefore can be applied to a broad class of problem in the domains of Laplace and Hankle transforms.

Application

We consider an infinite micropolar viscoelastic space in which a concentrated force of magnitude $F = \frac{-F_0 \delta(r) \delta(t)}{2\pi r}$ acting in the direction of the z -axis at the origin of the cylindrical co-ordinate system. The problem is axisymmetric w.r.t. the z -axis. The boundary conditions at the plane $z = 0$ are given by

$$u_r(r, 0^+, t) - u_r(r, 0^-, t) = 0, \quad u_z(r, 0^+, t) - u_z(r, 0^-, t) = 0, \quad (37)$$

$$\phi_\theta(r, 0^+, t) - \phi_\theta(r, 0^-, t) = 0, \quad (38)$$

$$m_{z\theta}(r, 0^+, t) - m_{z\theta}(r, 0^-, t) = 0, \quad (39)$$

$$t_{zr}(r, 0^+, t) - t_{zr}(r, 0^-, t) = 0, \quad (40)$$

$$t_{zz}(r, 0^+, t) - t_{zz}(r, 0^-, t) = -\frac{F_0 \delta(r) \delta(t)}{2\pi r} \quad (41)$$

Applying the Laplace and Hankel transforms to eqn. (37)–(41),

we get

$$\tilde{u}_r(\xi, 0^+, p) - \tilde{u}_r(\xi, 0^-, p) = 0, \quad \tilde{u}_z(\xi, 0^+, p) - \tilde{u}_z(\xi, 0^-, p) = 0, \quad (42)$$

$$\tilde{\phi}_\theta(\xi, 0^+, p) - \tilde{\phi}_\theta(\xi, 0^-, p) = 0, \quad (43)$$

$$\tilde{m}_{z\theta}(\xi, 0^+, p) - \tilde{m}_{z\theta}(\xi, 0^-, p) = 0, \quad (44)$$

$$\tilde{t}_{zr}(\xi, 0^+, p) - \tilde{t}_{zr}(\xi, 0^-, p) = 0, \quad (45)$$

$$\tilde{t}_{zz}(\xi, 0^+, p) - \tilde{t}_{zz}(\xi, 0^-, p) = -\frac{F_o}{2\pi}, \quad (46)$$

The transformed displacements, microrotation, couple stress and stresses are given for $z \geq 0$ by

$$\tilde{u}_r(\xi, z, p) = -[a_1 q_1 B_4 \exp(-q_1 z) + a_2 q_2 B_5 \exp(-q_2 z) + a_3 q_3 B_6 \exp(-q_3 z)], \quad (47)$$

$$\tilde{u}_z(\xi, z, p) = b_1 B_4 \exp(-q_1 z) + b_2 B_5 \exp(-q_2 z) + b_3 B_6 \exp(-q_3 z) \quad (48)$$

$$\tilde{\phi}_\theta(\xi, z, p) = -\xi[B_4 \exp(-q_1 z) + B_5 \exp(-q_2 z) + B_6 \exp(-q_3 z)], \quad (49)$$

$$\tilde{m}_{z\theta}(\xi, z, p) = s_7 \xi[q_1 B_4 \exp(-q_1 z) + q_2 B_5 \exp(-q_2 z) + q_3 B_6 \exp(-q_3 z)], \quad (50)$$

$$\begin{aligned} \tilde{t}_{rr}(\xi, z, p) = & (a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}) B_4 \exp(-q_1 z) \\ & + (a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}) B_5 \exp(-q_2 z) \\ & + (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) B_6 \exp(-q_3 z) \end{aligned} \quad (51)$$

$$\begin{aligned} \tilde{t}_{zz}(\xi, z, p) = & -[q_1 (b_1 s_6 + \xi a_1 s_5) B_4 \exp(-q_1 z) + q_2 (b_2 s_6 + \xi a_2 s_5) B_5 \exp(-q_2 z) \\ & + q_3 (b_3 s_6 + \xi a_3 s_5) B_6 \exp(-q_3 z)], \end{aligned} \quad (52)$$

and for $z \leq 0$ by

$$\tilde{u}_r(\xi, z, p) = a_1 q_1 B_1 \exp(q_1 z) + a_2 q_2 B_2 \exp(q_2 z) + a_3 q_3 B_3 \exp(q_3 z), \quad (53)$$

$$\tilde{u}_z(\xi, z, p) = b_1 B_1 \exp(q_1 z) + b_2 B_2 \exp(q_2 z) + b_3 B_3 \exp(q_3 z) \quad (54)$$

$$\tilde{\phi}_\theta(\xi, z, p) = -\xi[B_1 \exp(q_1 z) + B_2 \exp(q_2 z) + B_3 \exp(q_3 z)], \quad (55)$$

$$\tilde{m}_\theta(\xi, z, p) = -s_7 \xi[q_1 B_1 \exp(q_1 z) + q_2 B_2 \exp(q_2 z) + q_3 B_3 \exp(q_3 z)], \quad (56)$$

$$\begin{aligned} \tilde{t}_x(\xi, z, p) = & (a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}) B_1 \exp(q_1 z) + (a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}) B_2 \exp(q_2 z) + \\ & (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) B_3 \exp(q_3 z) \end{aligned} \quad (57)$$

$$\begin{aligned} \tilde{t}_{zz}(\xi, z, p) = & q_1 (b_1 s_6 + \xi a_1 s_5) B_1 \exp(q_1 z) + q_2 (b_2 s_6 + \xi a_2 s_5) B_2 \exp(q_2 z) + q_3 (b_3 s_6 + \\ & \xi a_3 s_5) B_3 \exp(q_3 z), \end{aligned} \quad (58)$$

where,

$$\begin{aligned} s_5 &= \frac{\lambda_1 \mu_1}{\rho K_1 h^2 \omega^2}, & s_6 &= \frac{(\lambda_1 + 2\mu_1 + K_1) \mu_1}{\rho K_1 h^2 \omega^2}, & s_7 &= \frac{\gamma_1 \mu_1}{\rho K_1 h^4 \omega^2}, \\ s_8 &= \frac{(\mu_1 + K_1) \mu_1}{\rho K_1 h^2 \omega^2}, & s_9 &= \frac{\mu_1^2}{\rho K_1 h^2 \omega^2}, & s_{10} &= \frac{\mu_1}{\rho h^2 \omega^2} \end{aligned}$$

Using conditions (42)–(46) in eqns. (47)–(48), we obtain

$$a_1 q_1 (B_1 + B_4) + a_2 q_2 (B_2 + B_5) + a_3 q_3 (B_3 + B_6) = 0, \quad (59)$$

$$(B_1 - B_4) + (B_2 - B_5) + (B_3 - B_6) = 0, \quad (60)$$

$$b_1 (B_1 - B_4) + b_2 (B_2 - B_5) + b_3 (B_3 - B_6) = 0 \quad (61)$$

$$q_1 (B_1 + B_4) + q_2 (B_2 + B_5) + q_3 (B_3 + B_6) = 0 \quad (62)$$

$$[a_1 q_1^2 s_8 - \xi b_1 s_9 + \xi s_{10}] (B_1 - B_4) + [a_2 q_2^2 s_8 - \xi b_2 s_9 + \xi s_{10}] (B_2 - B_5)$$

$$+ (a_3 q_3^2 s_8 - \xi b_3 s_9 + \xi s_{10}) (B_3 - B_6) = 0 \quad (63)$$

$$q_1 (b_1 s_6 + \xi a_1 s_5) (B_1 + B_4) + q_2 (b_2 s_6 + \xi a_2 s_5) (B_2 + B_5) \\ + q_3 (b_3 s_6 + \xi a_3 s_5) (B_3 + B_6) = \frac{F_o}{2\pi} \quad (64)$$

Solving system of eqns. (59) – (60), we obtain

$$B_1 = B_4 \frac{F_o (a_3 - a_2)}{4\pi q_1 \Delta_1}, \quad (65)$$

$$B_5 = B_5 \frac{F_o (a_1 - a_3)}{4\pi q_2 \Delta_1}, \quad (66)$$

$$B_3 = B_6 \frac{F_o (a_2 - a_1)}{4\pi q_3 \Delta_1}, \quad (67)$$

where

$$\Delta_1 = s_6 [(a_2 b_3 - a_3 b_2) + (a_3 b_1 - a_1 b_3) + (a_1 b_2 - a_2 b_1)].$$

Thus the components \tilde{u}_r , \tilde{u}_z , $\tilde{\phi}_\theta$, $\tilde{m}_{z\theta}$, \tilde{t}_{rz} , and \tilde{t}_{zz} have been determined in the transform domain and these enable us to find the displacements, microrotation, couple stress and forces stress.

Inversion of Transforms

The transformed displacements and stresses are functions of z , the parameters of Laplace and Hankel transforms p and ξ respectively, and hence are of the form $f(\xi, z, p)$ in the physical domain, first we invert the Hankel transform using

$$\bar{f}(r, z, p) = \int_0^{\infty} \xi \bar{f}(\xi, z, p) J_n(\xi r) d\xi$$

Thus, expression (68) gives us the Laplace $\bar{f}(r, z, p)$ of the function $f(r, z, t)$. We invert the Laplace transform by using the inversion technique as used in Kumar and Choudhary²¹

Numerical Results and Discussion

Following Gauthier²², we take the following values of relevant parameters for the case of aluminum epoxy composite as

$$\begin{aligned} \rho &= 2.19 \text{ g/cm}^3, & \lambda &= 7.59 \times 10^{10} \text{ dyne/cm}^2, \\ \mu &= 1.89 \times 10^{10} \text{ dyne/cm}^2, & K &= 0.0149 \times 10^{10} \text{ dyne/cm}^2, \\ \gamma &= 0.0268 \times 10^{10} \text{ dyne}, & j &= .00196 \text{ cm}^2, \end{aligned}$$

For a particular model of micropolar viscoelastic solid the relevant parameters are expressed as

$$\chi = \chi (1 + iQ_i^{-1}) \quad i = 1, 2, 3, 4 \text{ for } \chi = \lambda, \mu, K, \gamma \text{ respectively}$$

where,

$$Q_1 = 0.05, \quad Q_2 = 0.01 \quad Q_3 = 0.015 \quad Q_4 = 0.1.$$

The comparison of values of dimensionless normal displacement $U_z [= (2\pi u_z / F_0)]$ and couple stress $M_{z\theta} [= (2\pi M_{z\theta} / F_0)]$ for micropolar elastic solid (ME) and micropolar viscoelastic solid (MVE) have been studied. The computations were carried out for two values of dimensionless time 0.05 and 0.10 and for $h = 1$ at $z = 1.0$ in the range $0 \leq r \leq 10$. The solid lines [—] in graphs represent the variations for time 0.05 and the dashed [----] represent the variations for time 0.10. For both the times, solid or dashed lines with center symbols represents the variations for ME, whereas without center symbols are for MVE.

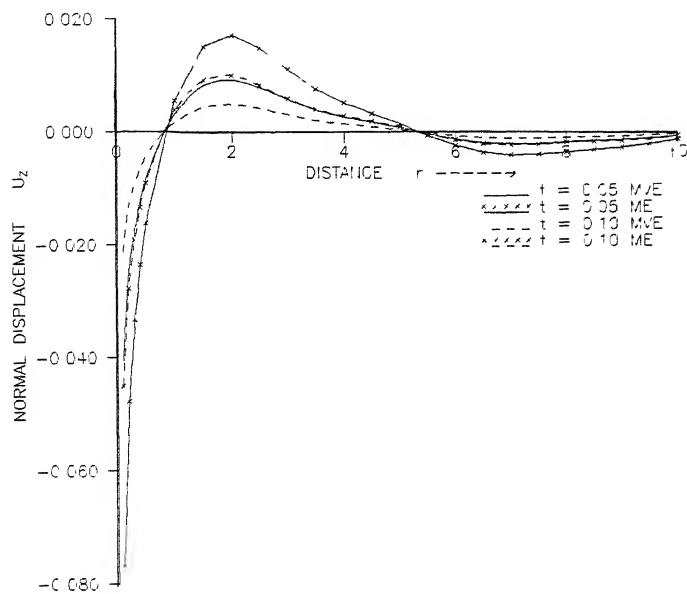


Fig. 1— Variations of normal displacement $U_z(r,1)(=u_z2\pi/F_0)$ with distance r

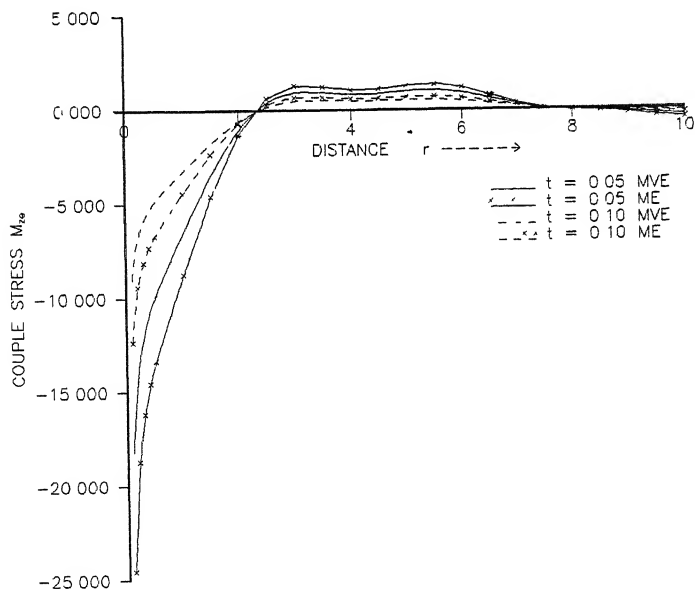


Fig. 2— Variations of couple stress $M_{x\theta}(r,1)(=m_{x\theta}2\pi/F_0)$ with distance r .

Fig. 1 shows the variations of normal displacement U_z with r . In the range $0 \leq r \leq 1$ and $5.5 \leq r \leq 10$ the values of U_z for time 0.50 are less in comparison with those for time 0.10 whereas in the range $1 \leq r \leq 5.5$ the time 0.05 are more than for time 0.10 for both MVE and ME. For fixed time 0.05 the values of U_z for MVE are more than those for ME in ranges $0 \leq r \leq 1$ and $5.5 \leq r \leq 10$ and less in the range $1 \leq r \leq 5.5$. The similar trends for time 0.10 have been shown.

Fig. 2 shows the variations of couple stress $M_{z\theta}$ with r . The values of $M_{z\theta}$ have been taken by multiplying their original values with 10^3 . In the ranges $(0 \leq r \leq 2)$ and $7 \leq r \leq 9$ the values of $M_{z\theta}$ for time 0.05 are less than the values for time 0.10 and in the ranges $2 \leq r \leq 7$ and $9 \leq r \leq 10$ the values for time 0.05 are more than those for time 0.10 for both MVE and ME. For fixed time 0.05 the values of $M_{z\theta}$ for MVE are more than those for ME in the ranges $0 \leq r \leq 2$ and $(7 \leq r \leq 10)$ and less for ME in the range $2 \leq r \leq 7$. The similar trends for time 0.10 have been shown.

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Kelvin-Helmholtz instability of two viscous superposed conducting fluids

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Abstract

The Kelvin-Helmholtz instability of two superposed viscous conducting fluids in a uniform vertical magnetic field is discussed in the presence of effects of surface tension and permeability of porous medium. The dispersion relation has been derived through normal mode technique and solved numerically. The streaming velocity is found to have a destabilizing influence while viscosity, surface tension and permeability of the medium have all stabilizing influence on the growth rate of unstable mode of disturbance.

(**Keywords** Kelvin-Helmholtz instability/surface tension/ viscosity/porous medium)

Introduction

The problem of the Kelvin-Helmholtz discontinuity between two superposed fluids is of prime importance in various astrophysical, geophysical and laboratory situations. The Kelvin-Helmholtz discontinuity arises when air is blown over mercury or when highly ionized hot plasma is surrounded by a slightly cold gas or when a meteor enters the earth's atmosphere. Chandrasekhar¹ has given a detailed account of the various investigations of this problem as investigated by different researchers for incompressible fluids. For the case of a low - β magnetized plasma in the presence of effects of compressibility, D' Angelo² found that a velocity difference between adjacent field-aligned flows, on the order of the ion-acoustic speed c_s , is sufficient for instability. The results of his calculations were in agreement with experimental findings in a Q-machine (D' Angelo and von Geoler³). Gerwin⁴ has examined the stability problem of the non-conducting streaming gas flowing over an incompressible conducting fluid. Kalra, Lister and Hosking⁵ have investigated Kelvin-Helmholtz instability of superposed fluids in the presence of the effects of magnetic resistivity while Bhatia and Steiner⁶ have analysed this problem for partially ionized plasmas. Shivamoggi⁷ has studied the effect of finite magnetic resistivity on the Kelvin-Helmholtz instability of superposed plasmas. Sengar⁸ has analysed the stability of

superposed gravitating streams in a uniform vertical magnetic field in the presence of effects of magnetic resistivity. Mehta and Bhatia⁹ investigated Kelvin-Helmholtz instability of two viscous, superposed, rotating and conducting fluids. Singh and Khare¹⁰ have investigated the stability of two semi-infinite homogeneous gravitating streams of infinite conductivity under uniform horizontal magnetic field and uniform rotation. Eldabe and Hassan¹¹ have examined the effects of surface tension and finite magnetic resistivity on the Kelvin-Helmholtz instability of superposed fluids in a horizontal magnetic field. Bhatia and Hazarika¹² discussed this stability problem for superposed viscous gravitating fluids. The importance of the Kelvin-Helmholtz problem has been demonstrated recently by Benjamin and Bridges¹³⁻¹⁴ who have given an excellent reappraisal of the classic Kelvin-Helmholtz problem in hydrodynamics. They have shown that the problem admits of a canonical Hamiltonian formulation and obtained several new results. More recently Sharma and Kumar¹⁵ have studied the Rayleigh-Taylor instability of two superposed conducting Walter's B' elasticoviscous fluids in hydromagnetics while Allah¹⁶ has investigated the effects of magnetic field and heat and mass transfer on the Kelvin-Helmholtz instability of superposed fluids.

The flow through porous medium has been of considerable importance in recent years particularly among geophysical fluid dynamicists and petroleum engineers. The physical properties of the comets, meteorites and interplanetary dust strongly suggest the significance of the effects of porosity in astrophysical context (Mc Donnell¹⁷). Several authors¹⁸⁻²² have investigated the effects of permeability of the porous medium on different stability problems.

The aim of this paper is to study the Kelvin-Helmholtz discontinuity between two viscous conducting fluids in a uniform vertical magnetic field through a porous medium in the presence of the effects of surface tension.

Perturbation Equations

Consider the motion of an incompressible, infinitely conducting viscous fluid of variable viscosity $\mu_0(z)$ through porous medium having a streaming velocity U along x -direction. The magnetic field is taken to be uniform and vertical. If we denote by \vec{u} (u, v, w), \vec{h} (h_x, h_y, h_z), $\delta\rho$ and δp , the perturbations in Darcian velocity, magnetic field \vec{H} , density ρ and pressure p respectively, then the linearized perturbation equations appropriate to the problem are

$$\frac{\rho}{\epsilon} \frac{\partial \vec{u}}{\partial t} + \frac{\rho}{\epsilon} (\vec{U} \cdot \nabla) \vec{u} = -\nabla \delta p + \vec{g} \delta \rho + (\nabla \times \vec{h}) \times \vec{H} + \frac{\mu}{\epsilon} \nabla^2 \vec{u}$$

$$-\frac{\mu}{\lambda}\bar{u} + \Sigma \left[T_s \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \delta z_s \right] \delta(z - z_s) \quad (1)$$

$$\in \frac{\partial \bar{h}}{\partial t} + (\bar{U} \cdot \nabla) \bar{h} = (\bar{H} \cdot \nabla) \bar{u} \quad (2)$$

$$\in \frac{\partial}{\partial t} \delta \rho + (\bar{U} \cdot \nabla) \delta \rho + (\bar{u} \cdot \nabla) \rho = 0 \quad (3)$$

$$\in \frac{\partial}{\partial t} \delta z_s + w_s \quad (4)$$

$$\nabla \cdot \bar{u} = 0 \quad (5)$$

$$\nabla \cdot \bar{h} = 0 \quad (6)$$

As stated above, we take streaming velocity $\bar{U} = (U, 0, 0)$ and magnetic field $\bar{H} = (0, 0, H_0)$. Here, T , μ and $\bar{g} = (0, 0, -g)$ denote surface tension, coefficient of viscosity and acceleration due to gravity respectively. In equation (1), $\delta(z - z_s)$ denotes Dirac's δ function, λ denotes permeability of porous medium and \in is the medium porosity.

Analyzing the disturbances in terms of normal modes, we assume that the perturbed quantities have dependence on space coordinates x , z and time t of the form

$$F(z) \exp(ik_x x + nt) \quad (7)$$

where $F(z)$ is some function of z , k_x is the wave number along x -direction and n (may be complex) is the frequency of the harmonic disturbance.

Using equation (7) in equations (1) to (6), we get

$$\frac{\rho}{\in} (n + ik_x U) u = -ik_x \delta p + H_0 D h_x - H_0 i k_x h_z + \frac{\mu}{\in} (D^2 - k^2) u - \frac{\mu}{\lambda} u \quad (8)$$

$$\frac{\rho}{\epsilon}(n + ik_x U) v = H_0 D h_y + \frac{\mu}{\epsilon} (D^2 - k_x^2) v - \frac{\mu}{\lambda} v \quad (9)$$

$$\frac{\rho}{\epsilon}(n + ik_x U) w = -D \delta p - g \delta \rho + \frac{\mu}{\epsilon} (D^2 - k_x^2) w - \frac{\mu}{\lambda} w - \frac{k_x^2 T}{n \epsilon} \delta(z - z_s) w \quad (10)$$

$$\epsilon (n + ik_x U) h_x = H_0 D u \quad (11)$$

$$\epsilon (n + ik_x U) h_y = H_0 D v \quad (12)$$

$$\epsilon (n + ik_x U) h_z = H_0 D w \quad (13)$$

$$(n + ik_x U) \delta \rho = -(D \rho) w \quad (14)$$

$$ik_x h_x + D h_z = 0 \quad (15)$$

$$ik_x u + D w = 0 \quad (16)$$

where

$$D = \frac{d}{dz}$$

Eliminating some of the variables from the above equations, we obtain an equation in w as

$$\begin{aligned} & \frac{n' \rho}{\epsilon} [k_x^2 \rho w - D(\rho D w)] - \frac{g k_x^2}{n' \epsilon} w + \frac{H_0^2}{n' \epsilon} (D^2 - k_x^2) D^2 w \\ & + \frac{\mu}{\epsilon} (D^2 - k_x^2)^2 w - \frac{\mu}{\lambda} (D^2 - k_x^2) w + \frac{k_x^4}{n' \epsilon} \delta(z - z_s) w = 0 \end{aligned} \quad (17)$$

where we have written $n' = (n + ik_x U)$.

Two Superposed Streaming Fluids

We now consider the case when two superposed fluids of uniform viscosities μ_1 and μ_2 , uniform densities ρ_1 and ρ_2 , magnetic fields H_1 and H_2 and with streaming velocities U_1 and U_2 are separated by a horizontal boundary at the interface $z = 0$. Therefore, in both the regions $z < 0$ and $z > 0$ of constant densities, equation (17) becomes

$$(D^2 - k_x^2) (D^2 - M^2) w = 0 \quad (18)$$

where

$$M^2 = \frac{k_x^2 n' \nu}{n' \nu + V_A^2} \left(1 + \frac{\epsilon}{\lambda k_x^2} + \frac{n'}{\nu k_x^2} \right) \quad (19)$$

In equation (19), $\nu = \frac{\mu}{\rho}$ is the coefficient of kinematic viscosity while $V_A^2 = \frac{H_0^2}{\rho}$ is the Alfvén velocity

Now, seeking the solutions of equation (18), which remain bounded in the two regions, we obtain

$$w_1 = A_1 n'_1 e^{k_x z} + B_1 n'_1 e^{M_1 z}; \quad z < 0 \quad (20)$$

$$w_2 = A_2 n'_2 e^{-k_x z} + B_2 n'_2 e^{-M_2 z}; \quad z > 0 \quad (21)$$

where A_1, A_2, B_1 and B_2 are constants of integration and M_1 and M_2 are square roots of equation (19) and

$$n'_1 = n + ik_x U_1; \quad n'_2 = n + ik_x U_2 \quad (22)$$

and

$$M_1^2 = \frac{k_x^2 n'_1 v_1}{n'_1 v_1 + V_1^2} \left[1 + \frac{\epsilon_1}{\lambda_1 k_x^2} + \frac{n'_1}{v_1 k_x^2} \right] \quad (23)$$

$$M_2^2 = \frac{k_x^2 n'_2 v_2}{n'_2 v_2 + V_2^2} \left[1 + \frac{\epsilon_2}{\lambda_2 k_x^2} + \frac{n'_2}{v_2 k_x^2} \right] \quad (24)$$

are the values of M_1 and M_2 for the two regions. Since n' is complex, M_2 is therefore complex and consequently M_1 and M_2 are complex. In writing the solutions (20) and (21) it is assumed that M_1 and M_2 are so defined that their real parts are positive.

The above solutions must satisfy certain boundary conditions. These conditions require that at an interface $z = 0$,

$$w, Dw \text{ and } \mu (D^2 + k_x^2) w \quad (25a, b, c)$$

must be continuous.

If we integrate equation (17) across the interface $z = 0$, we obtain another condition

$$\begin{aligned} & \left[n'_2 \rho_2 Dw_2 - \mu_2 (D^2 - k_x^2) Dw_2 - \frac{H_2^2}{n'_2} (D^2 - k_x^2) Dw_2 + \frac{\mu_2 \epsilon}{\lambda} Dw_2 \right]_{z=0} \\ & - \left[n'_1 \rho_2 Dw_1 - \mu_1 (D^2 - k_x^2) Dw_1 - \frac{H_1^2}{n'_1} (D^2 - k_x^2) Dw_1 + \frac{\mu_1 \epsilon}{\lambda} Dw_1 \right]_{z=0} \\ & = -k_x^2 \left\{ g \left(\frac{\rho_2}{n'_2} - \frac{\rho_1}{n'_1} \right) - k_x^2 T \right\} w_0 - 2 k_x^2 (\mu_2 - \mu_1) (Dw)_0 \end{aligned} \quad (26)$$

where w_0 and $(Dw)_0$ are the unique values of these quantities at $z = 0$. If we apply the conditions (25) and (26) to the solutions (20) and (21), we obtain

$$A_1 + B_1 = A_2 + B_2 \quad (27)$$

$$k_x A_1 + M_1 B_1 = -k_x A_2 - M_2 B_2 \quad (28)$$

$$\begin{aligned} & \mu_1 [2k_x^2 A_1 + (M_1^2 + k_x^2) B_1] \\ &= \mu_2 [2k_x^2 A_2 + (M_2^2 + k_x^2) B_2] \end{aligned} \quad (29)$$

$$\begin{aligned} & A_2 (-k_x \rho_2 n'_2) - \frac{H_2^2 k_x^2}{n'_2} M_2 B_2 + A_1 (-k_x \rho_1 n'_1) - \frac{H_1^2 k_x^2}{n'_1} M_1 B_1 \\ &= -\frac{k_x^2}{2} \left[g \left(\frac{\rho_2}{n'_2} - \frac{\rho_1}{n'_1} \right) - k_x^2 T \right] (A_1 + B_1 + A_2 + B_2) \\ & - k_x^2 (\mu_2 - \mu_1) (k_x A_1 + M_1 B_1 - k_x A_2 - M_2 B_2) \end{aligned} \quad (30)$$

Eliminating the constants A_1, B_1, A_2 and B_2 from equations (27) to (30) and writing

$$R = \frac{gk_x}{2} \left[\left(\frac{\alpha_2}{n'_2} - \frac{\alpha_1}{n'_1} \right) - \frac{k_x^2 T}{g(\rho_1 + \rho_2)} \right] \quad (31)$$

$$C = k_x^2 (\alpha_2 v_2 - \alpha_1 v_1), \quad \alpha_{1,2} = \frac{\rho_{1,2}}{\rho_1 + \rho_2} \quad (32)$$

we obtain the following characteristic equation

$$\begin{aligned} & (M_1 - k_x) \left[2k_x^2 (\alpha_1 v_1 - \alpha_2 v_2) \left\{ \frac{k_x V_2^2}{n'_2} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n'_2 \right\} \right. \\ & \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \{ \alpha_2 n'_2 + \alpha_1 n'_1 - 2R \} \right] \end{aligned}$$

$$\begin{aligned}
& -2k_x \left[\alpha_1 v_1 (M_1^2 - k_x^2) \left\{ \frac{k_x V_2^2}{n_2'} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n_2' \right\} \right. \\
& \quad \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\} \right] \\
& -2k_x \left[\alpha_1 v_1 (M_1^2 - k_x^2) \left\{ \frac{k_x V_2^2}{n_2'} M_2 + \frac{C}{k_x} (M_2 - k_x) - \alpha_2 n_2' \right\} \right. \\
& \quad \left. + \alpha_2 v_2 (M_2^2 - k_x^2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\} \right] \\
& + (M_2 - k_x) [\alpha_1 v_1 (M_1^2 - k_x^2) \{\alpha_2 n_2' + \alpha_1 n_1' - 2R\} \\
& - 2k_x^t (\alpha_1 v_1 - \alpha_2 v_2) \left\{ \frac{k_x V_1^2}{n_1'} M_1 + \frac{C}{k_x} (M_1 - k_x) - \alpha_1 n_1' \right\}] = 0 \quad (33)
\end{aligned}$$

wherein the subscript A on Alfvén velocity V_A has been dropped for convenience. The dispersion relation (33) is quite complex. We therefore, consider the case of two highly viscous and highly permeable fluids for then we can write

$$M_1 = k + \frac{\alpha_1 n_1' + \alpha_1 v_1 \frac{\epsilon_1}{\lambda_1} - \frac{k^2 V_1^2}{n_1'}}{2k \left[\alpha_1 v_1 + \frac{V_1^2}{2n_1'} \right]} \quad (34)$$

$$M_2 = k + \frac{\alpha_2 n_2' + \alpha_2 v_2 \frac{\epsilon_2}{\lambda_2} - \frac{k^2 V_2^2}{n_2'}}{2k \left[\alpha_2 v_2 + \frac{V_2^2}{2n_2'} \right]} \quad (35)$$

Now we consider the case of two streams, of equal Alfvén velocities and same kinematic viscosities and same permeabilities, flowing past each in opposite directions with equal velocities i.e.

$$\begin{aligned} V_1 = V_2 = V, \quad v_1 = v_2 = v, \quad U_1 = U, \quad U_2 = -U \\ \epsilon_1 = \epsilon_2 = \epsilon, \quad \lambda_1 = \lambda_2 = \lambda \end{aligned} \quad (36)$$

Now substituting the values of M_1 and M_2 from equations (34) and (35), the dispersion relation (33) becomes, on writing $k_x = k$, the ninth degree polynomial

$$\sum_{i=0}^9 A_i n^i = 0 \quad (37)$$

where the coefficients A_i ($i = 0$, to 9) are given in the Appendix.

Discussion

The dispersion relation given by equation (37) is quite complicated particularly as the coefficients A_i 's are complex. We have therefore solved the dispersion relation numerically for different values of the parameters characterizing viscosity, streaming motion, surface tension and permeability of the medium. The dispersion relation was of course first non-dimensionalized by measuring n , v , B , V , Q and U in terms of \sqrt{g} . For numerical evaluation of the roots of dispersion relation we have taken $\alpha_1 = 0.25$, $\alpha_2 = 0.75$ (the unstable configuration), Alfvén velocity $V = 1$ in all the calculations.

These calculations are presented in Figs. 1 to 4 where the growth rate (positive real part of n) is plotted against the wave number k for several values of v , U , B and Q . In Fig. 1, the growth rate is given against the wave number for v (viscosity) = 0.1, 0.2, 0.3 taking fixed values of B (surface tension) = 0.1, U (streaming velocity) = 1, Q (permeability) = 0.05. From the Fig. 1 we find that the growth rate decreases on increasing the viscosity for same values of the wave number. We thus find that viscosity has stabilizing influence on the Kelvin-Helmholtz instability of the superposed fluids. In Fig. 2 we have given the variation of the growth rate against the wave number for the values of streaming velocity $U = 2.1, 2.2, 2.3, 2.4$. In these curves also the values of the other parameters have been kept fixed. From Fig. 2 we

find that the streaming velocity has a destabilizing influence as the growth rate increases with increasing streaming velocity for same values of the wave number. Fig. 3 depicts the variation of the growth rate with surface tension. The curves in the Fig. 3 clearly show that the growth rate decreases with increasing values of B , the parameter characterizing effect of the surface tension. As the growth rate decreases on increasing the values of B for same wave number k . The effect of surface tension is thus stabilizing on the growth rate of the unstable configuration. Fig. 4 gives the plot of growth rate against the wave number for the values of permeability parameter $Q = 0.2, 0.1, 0.05$. From Fig. 4, we find that the growth rate decreases on decreasing parameter Q . The effect of permeability is consequently stabilizing and/or the effect of porosity is destabilizing. These observations are in agreement with the earlier observations of several researchers on the different stability problems.

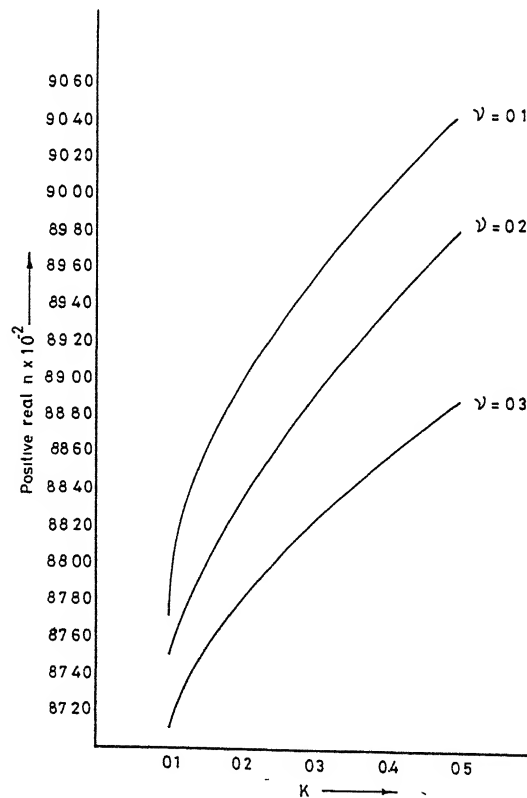


Fig. 1—Variation of growth rate n against wave number K for $v = 0.1, 0.2, 0.3$ taking $B = 0.1, U = 1.0, Q = 0.2$

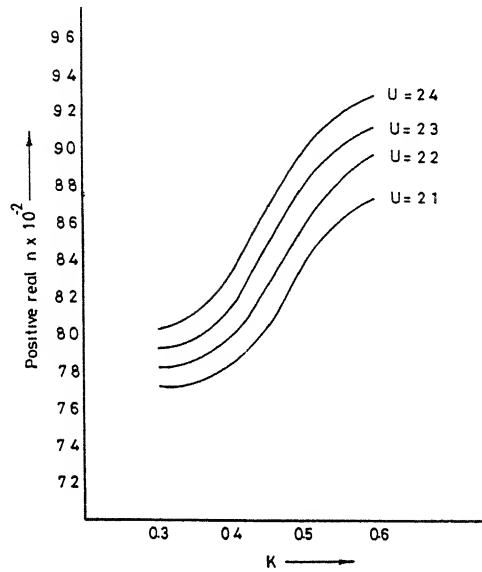


Fig. 2—Variation of growth rate n against wave number K for $U = 2.1, 2.2, 2.3, 2.4$ taking $\nu = 0.1, B = 1.0, Q = 0.05$

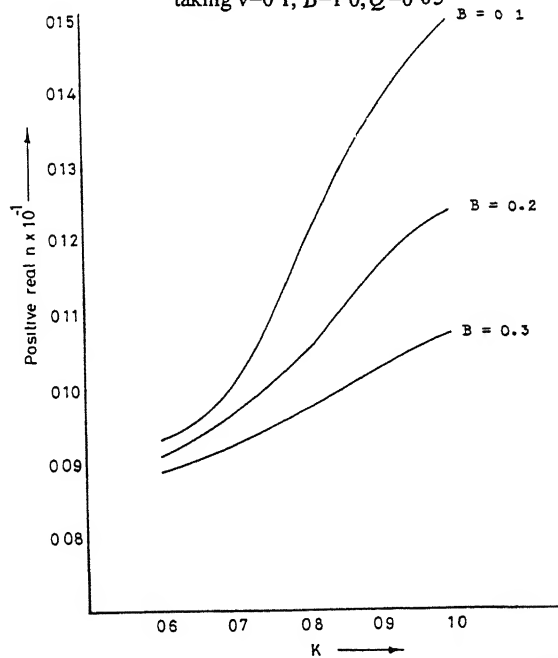


Fig. 3—Variation of growth rate n against wave number K for $B = 0.1, 0.2, 0.3$ taking $\nu = 0.1, U = 1.0, Q = 0.2$

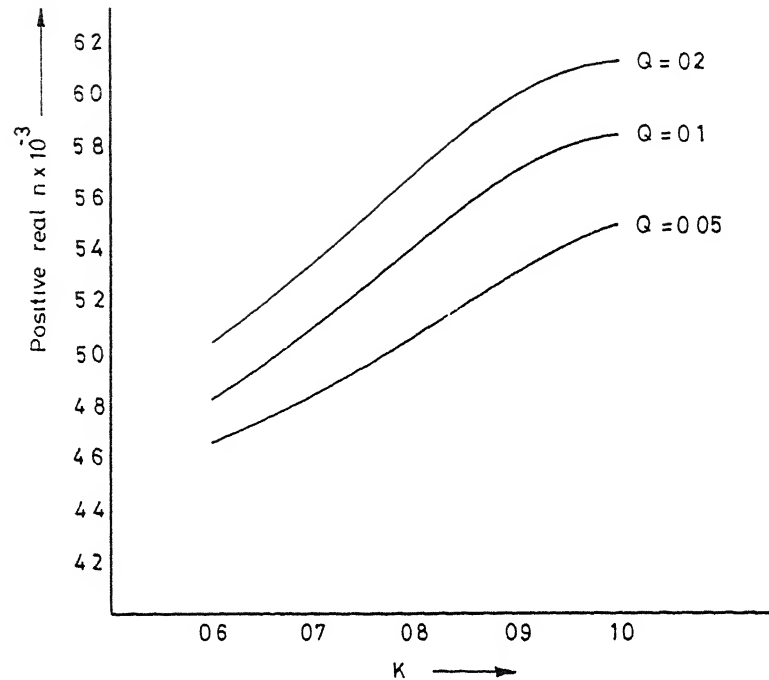


Fig 4-Variation of growth rate n against wave number K for $Q = 0.2, 0.1, 0.05$ taking $U=1.0, B=0.1$

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APPENDIX

$$A_9 = 2\alpha_1^2 \alpha_2^2 \gamma^2$$

$$A_8 = \alpha_1 \alpha_2 \gamma \left\{ -21\alpha_1 \alpha_2 \gamma U k (\alpha_2 - \alpha_1) + 4\alpha_1 \alpha_2 \gamma^2 (Q + 2\alpha_1 k^2) \right. \\ \left. + 2\alpha_1 \alpha_2 k^3 B \gamma + 2V^2 (1 - 2\alpha_1 \alpha_2) \right\}$$

$$A_7 = 21Uk \gamma \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) [2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (2 - \alpha_1 \alpha_2)] \\ + 4\alpha_1^2 \alpha_2^2 \gamma^2 k^2 U^2 + \alpha_1 \alpha_2 \left\{ \alpha_1 \alpha_2 \gamma^4 Q (Q + 2k^2 (3\alpha_1 - \alpha_2)) \right. \\ \left. + 4\alpha_1 \alpha_2 \gamma^3 k^3 B Q + \gamma^2 V^2 [4Q(1 - \alpha_1 \alpha_2) - k^2 (4\alpha_1 \alpha_2 (8 - 12\alpha_1 \alpha_2 \right. \\ \left. + \alpha_2 - \alpha_1) - 6)] + 2\gamma k^3 B V^2 (1 - \alpha_1 \alpha_2) \right\}$$

$$A_6 = 1Uk \alpha_1 \alpha_2 \left\{ -4\gamma^2 k^2 U^2 \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \right. \\ \left. - Q(\alpha_2 - \alpha_1)] - 4\alpha_1^2 \alpha_2 \gamma^3 k^3 B Q - 2\alpha_1 \alpha_2 \gamma^2 k + \gamma^2 V^2 \{ 3(\alpha_2 - \alpha_1) \right. \\ \left. \cdot (2k^2 - Q(2 - \alpha_1 \alpha_2)) + 2k^2 [(\alpha_2 - \alpha_1)(3\alpha_1 \alpha_2 - 2) + 2 - 9\alpha_1 \alpha_2] \right. \\ \left. + 2Q(\alpha_1^2 \alpha_2 - 1) \right\} - 2k^3 B \gamma V^2 - V^4 (\alpha_2 - \alpha_1) \} \\ + 2\alpha_1 \alpha_2 \gamma k^2 U^2 \left\{ 2\alpha_1 \alpha_2 \gamma^2 (3Q + 8\alpha_1 k^2) + 4\alpha_1 \alpha_2 k^3 B \gamma + V^2 (\alpha_1 \alpha_2 + 2) \right\} \\ - k^2 \gamma V^4 (2 - 7\alpha_1 \alpha_2 + 2\alpha_1^2 \alpha_2^2) - 2\alpha_1^2 \alpha_2^2 \gamma^3 k Q (\alpha_2 - \alpha_1) \\ + \alpha_1 \alpha_2 \gamma V^2 \left\{ k \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + V^2 (Q - 3k^2) + 2\gamma k^3 B (Q(1 - \alpha_1 \alpha_2) - k^2) \right. \\ \left. + \gamma^2 [Q^2 (2 - 5\alpha_1 \alpha_2) + 2Qk^2 [2(\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 1) - 6\alpha_1 \alpha_2 + 1] - 8k^4 \alpha_1] \right\} +$$

$$\begin{aligned}
& + \alpha_1 \alpha_2 \left\{ k^3 B V^4 + \gamma^3 Q [V^2 (3\alpha_1 \alpha_2 Q - 4k^2 (\alpha_2 - \alpha_1) (1 - 2\alpha_1 \alpha_2)) \right. \\
& - 2\alpha_1 \alpha_2 k (\alpha_2 - \alpha_1) + 2\alpha_1 \alpha_2 \gamma Q k^2 (k B - 2\gamma)] + \gamma V^2 [k (\alpha_2 - \alpha_1) \\
& \cdot (\alpha_1 \alpha_2 - 2) + V^2 (2k^2 \alpha_1 (2 - 3\alpha_1) + Q) + 2\gamma k^3 B Q (1 - \alpha_1 \alpha_2)] \left. \right\}
\end{aligned}$$

$$\begin{aligned}
A_5 = & 1kU \left\{ - 6\alpha_1 \alpha_2 k^2 U^2 \gamma (\alpha_2 - \alpha_1) [2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (2 - \alpha_1 \alpha_2)] \right. \\
& + 4k^2 \gamma V^4 (\alpha_2 - \alpha_1) (2 - 3\alpha_1 \alpha_2) + 2\alpha_1 \alpha_2 \gamma \left\{ V^4 (\alpha_2 - \alpha_1) (3k^2 - Q) \right. \\
& - 2\alpha_1 \alpha_2 \gamma^2 k Q + V^2 \left\{ \gamma^2 [Q^2 (\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 2) + 2k^2 Q (\alpha_2 - \alpha_1) \right. \\
& \cdot (1 - 2\alpha_1 \alpha_2) - 4\alpha_1 \alpha_2] - 16\alpha_1^2 \alpha_2 k^4] - 5\alpha_1 \alpha_2 k - 2\gamma k^3 B \\
& \cdot (\alpha_2 - \alpha_1) (Q - k^2) \left. \right\} \left. \right\} + 6\alpha_1^2 \alpha_2^2 \gamma^2 U^4 k^4 + \alpha_1 \alpha_2 k^2 U^2 \\
& \cdot \left\{ - \gamma^2 V^2 [Q (2 - 5\alpha_1 \alpha_2) - 2k^2 (1 - 2\alpha_1 \alpha_2)] + 3 \left\{ V^4 + \gamma^2 V^2 \right. \right. \\
& \cdot [Q (\alpha_1 \alpha_2 + 2) + 4k^2 (\alpha_1 \alpha_2 (\alpha_2 - \alpha_1 - 12\alpha_1 \alpha_2 + 7) - 1)] \\
& + 2\gamma k^3 B (2\alpha_1 \alpha_2 \gamma^2 Q + V^2 (1 - \alpha_1 \alpha_2)) + \gamma^4 Q (\alpha_1 \alpha_2 Q \\
& + 2\alpha_1 \alpha_2 k^2 (3\alpha_1 - \alpha_2)) \left. \right\} \left. \right\} + \alpha_1 \alpha_2 \left\{ V^4 [\gamma k^3 B (2Q - 3k^2) - 2V^2 k^2 \right. \\
& - k (\alpha_2 - \alpha_1)] + \gamma^4 k Q \left\{ 4V^2 k [k^2 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) + Q (\alpha_2 - \alpha_1) \right. \\
& \cdot (\alpha_1 \alpha_2 - 1) - \alpha_1 \alpha_2] - 2\alpha_1 \alpha_2 Q (\alpha_2 - \alpha_1) \left. \right\} + \gamma^2 V^2 \left\{ k (\alpha_2 - \alpha_1) \right. \\
& \cdot (3Q \alpha_1 \alpha_2 + 2(k^2 - 2Q)) + 2\gamma k^3 B Q (Q - k^2 (1 + 2\alpha_1 \alpha_2)) \\
& + V^2 [Q^2 + 4k^4 \alpha_1 (1 - 2\alpha_2) - k^2 Q (2(\alpha_1 \alpha_2 + \alpha_2 - \alpha_1) + 5)] \left. \right\} \left. \right\} \\
& + V^2 \left\{ k^2 V^4 (2\alpha_1 \alpha_2 - 1) - \gamma V^2 k^5 B (2 - 5\alpha_1 \alpha_2) + \right.
\end{aligned}$$

$$\begin{aligned}
& + \gamma^2 \left\{ \alpha_1^2 \alpha_2^2 k Q (\alpha_2 - \alpha_1) + v^2 k^2 [Q (5 \alpha_1 \alpha_2 - 2 \alpha_1^2 \alpha_2^2 - 2) \right. \\
& \left. + 2 k^2 [(\alpha_2 - \alpha_1)(1 - 5 \alpha_1 \alpha_2) + \alpha_1 \alpha_2 (2 \alpha_1 \alpha_2 - 7) + 1]] \right\} \\
A_4 = & i k U \left\{ - 6 \alpha_1^2 \alpha_2^2 \gamma^2 U^4 k^4 (\alpha_2 - \alpha_1) + \alpha_1 \alpha_2 k^2 U^2 \left\{ 5 \gamma^2 v^2 (\alpha_2 - \alpha_1) \right. \right. \\
& \cdot [2 k^2 - Q (2 - \alpha_1 \alpha_2)] + 2 \gamma^2 v^2 \left\{ k^2 [(\alpha_2 - \alpha_1)(3 \alpha_1 \alpha_2 - 2) \right. \\
& + (2 - 9 \alpha_1 \alpha_2)] + Q (\alpha_1^2 \alpha_2 - 1) \left. \right\} + 2 \alpha_1 \alpha_2 \gamma^4 Q [2 k^2 (2 \alpha_1 - \alpha_2) \\
& - Q (\alpha_2 - \alpha_1)] - 2 \alpha_1 \alpha_2 \gamma^2 k - (\alpha_2 - \alpha_1) v^4 - 2 k^3 B \gamma [2 \alpha_1^2 \alpha_2 \gamma^2 Q \\
& + v^2] \left. \right\} + \alpha_1 \alpha_2 \left\{ 2 k^2 v^6 (\alpha_2 - \alpha_1) + v^4 \left\{ \gamma^2 [(\alpha_2 - \alpha_1)(3 k^2 (Q - k^2) \right. \right. \\
& - Q^2) + 2 k^2 (4 \alpha_1 \alpha_2 - 1)(2(Q + k^2(k^2 - 1)) + k^2 Q)] - k - \gamma k^5 B (\alpha_2 - \alpha_1) \left. \right\} \\
& + \gamma^2 v^2 k [2 k (2 \alpha_1 \alpha_2 - 1) - 3 \alpha_1 \alpha_2 Q - \gamma k^3 B Q (Q - k^2) (\alpha_2 - \alpha_1)] \left. \right\} \\
& + 3 v^2 \left\{ - \alpha_1^2 \alpha_2^2 \gamma^2 k (3 Q - 4 k^2) + v^2 (\alpha_2 - \alpha_1) [v^2 k^2 (2 \alpha_1 \alpha_2 - 1) \right. \\
& + \gamma k^5 B (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 [Q (5 \alpha_1 \alpha_2 - 2) + 4 k^2 (1 + 2 \alpha_1 \alpha_2 (1 - 2 \alpha_1 \alpha_2)) \\
& + 2(Q + 2 \alpha_1^2 \alpha_2)]] \left. \right\} + 2 \alpha_1 \alpha_2 k^4 U^4 \gamma \left\{ 5 [2 \alpha_1 \alpha_2 \gamma^2 Q \right. \\
& + v^2 (2 - 5 \alpha_1 \alpha_2)] + 3 \alpha_1 \alpha_2 [2 \gamma^2 (Q + 4 \alpha_1 k^2) + 2 k^3 B \gamma + 3 v^2] \left. \right\} \\
& + k^2 U^2 \left\{ 5 \gamma v^4 k^2 (2 - 7 \alpha_1 \alpha_2 + 2 \alpha_1^2 \alpha_2^2) - 2 \alpha_1^2 \alpha_2^2 \gamma^3 k Q (\alpha_2 - \alpha_1) \right. \\
& + \alpha_1 \alpha_2 \gamma v^2 \left\{ k \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) + v^2 (Q - 3 k^2) + 2 \gamma k^3 B (Q (1 - \alpha_1 \alpha_2) - k^2) \right. \\
& + \gamma^2 [Q^2 (2 - 5 \alpha_1 \alpha_2) + 2 Q k^2 (2 (\alpha_2 - \alpha_1) (\alpha_1 \alpha_2 - 1) - 6 \alpha_1 \alpha_2 + 1) - 8 k^4 \alpha_1] \left. \right\} \\
& + 3 \alpha_1 \alpha_2 \left\{ k^3 B v^4 + \gamma^3 Q [v^2 (3 \alpha_1 \alpha_2 Q - 4 k^2 (\alpha_2 - \alpha_1) (1 - 2 \alpha_1 \alpha_2)) - \right.
\end{aligned}$$

$$\begin{aligned}
& - 2\alpha_1\alpha_2k(\alpha_2-\alpha_1)+2\alpha_1\alpha_2k^2Q\gamma(kB-2\gamma)+\gamma v^2[k(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2) \\
& + v^2(2k^2\alpha_1(2-3\alpha_1)+Q)+2\gamma k^3BQ(1-\alpha_1\alpha_2)]\}\} + \gamma v^2\{k^3B\gamma v^2 \\
& \cdot [2k^2Q((\alpha_2-\alpha_1)(1-\alpha_1\alpha_2)-2\alpha_1\alpha_2)+\alpha_1\alpha_2(Q^2+2k^4)] \\
& + k v^2(\alpha_2-\alpha_1)[2k^2(1-2\alpha_1\alpha_2)+\alpha_1\alpha_2(\alpha_2-\alpha_1)(Q-1)] \\
& + \alpha_1\alpha_2kQ\gamma^2(\alpha_2-\alpha_1)[2Q(1-\alpha_1\alpha_2)+k^2(3\alpha_1\alpha_2-2)]+v^4\{k^2Q \\
& \cdot [(\alpha_2-\alpha_1)(\alpha_1\alpha_2-1)-5\alpha_1\alpha_2]+2k^4[(\alpha_2-\alpha_1)(1-5\alpha_1\alpha_2)-3] \\
& + \alpha_1\alpha_2(2k^2+Q)\}\} + 2k^2\gamma^2v^2\{\alpha_1\alpha_2Q[(4\alpha_1\alpha_2-1)+Q(1-3(\alpha_2-\alpha_1) \\
& - 6\alpha_1\alpha_2)]+k^2[2\alpha_1\alpha_2(k^2(4\alpha_1\alpha_2-\alpha_2+\alpha_1)-2\alpha_1\alpha_2) \\
& + Q(1-2\alpha_1\alpha_2(3-4\alpha_1\alpha_2)+(\alpha_2-\alpha_1)(4\alpha_1\alpha_2-1))]\}\}
\end{aligned}$$

$$\begin{aligned}
A_3 = & iUk\left\{-26\alpha_1\alpha_2k^4U^4\gamma(\alpha_2-\alpha_1)[2\alpha_1\alpha_2\gamma^2Q+v^2(2-\alpha_1\alpha_2)]\right. \\
& + k^2U^2\left\{4\alpha_1\alpha_2\gamma\left\{v^4(\alpha_2-\alpha_1)(3k^2-Q)-2\alpha_1\alpha_2\gamma^2kQ\right.\right. \\
& + v^2\left\{\gamma^2[Q^2(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2)+2k^2Q((\alpha_2-\alpha_1)(1-2\alpha_1\alpha_2) \right. \\
& - 4\alpha_1\alpha_2)-16\alpha_1^2\alpha_2k^4]-5\alpha_1\alpha_2k-2\gamma k^3B(\alpha_2-\alpha_1)(Q-k^2)\}\}\} \\
& - 9\alpha_1\alpha_2\left\{v^4k^3B-2\alpha_1\alpha_2\gamma^3Qk[(\alpha_2-\alpha_1)+2\gamma^2Qk-\gamma k^3BQ] \right. \\
& + \gamma v^2\left\{v^2(2\alpha_1\alpha_2(Q+3k^2)-2k^2(\alpha_2-\alpha_1))+\gamma^2Q[2\alpha_1\alpha_2(Q+k^2) \right. \\
& + 4k^2(\alpha_2-\alpha_1)(2\alpha_1\alpha_2-1)]+2\gamma k^3BQ(1-\alpha_1\alpha_2)-k(\alpha_2-\alpha_1) \\
& \cdot (2-\alpha_1\alpha_2)\}\}\}\} + 2\left\{4\alpha_1\alpha_2\gamma v^4k^3(1-\alpha_1\alpha_2) - \right.
\end{aligned}$$

$$\begin{aligned}
& - v^2 \{ k^5 B v^4 (1-2\alpha_1 \alpha_2) + \gamma^3 \alpha_1^2 \alpha_2^2 k Q (3Q-4k^2) + \gamma v^2 k [k^2 \\
& \cdot (2-9\alpha_1 \alpha_2 + 4\alpha_1^2 \alpha_2^2) + \alpha_1 \alpha_2 Q] + \gamma^2 v^2 k^5 B [2Q(1-3\alpha_1 \alpha_2) \\
& - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1)] + \gamma k^2 v^4 \{ k^2 [(\alpha_2 - \alpha_1)(7\alpha_1 \alpha_2 - 2) \\
& + 4\alpha_1 \alpha_2 (1-4\alpha_1 \alpha_2) - 2] + (\alpha_2 - \alpha_1) [4k^4 (3\alpha_1 \alpha_2 - 1) - 4\alpha_1 \alpha_2 Q] \} \\
& - 2\alpha_1 \alpha_2 \gamma^3 v^2 k^2 Q [k^2 (2(\alpha_2 - \alpha_1) - 12\alpha_1 \alpha_2 + 11) + Q(\alpha_2 - \alpha_1)] \} \} \\
& + 4\alpha_1^2 \alpha_2^2 \gamma^2 k^6 U^6 + \alpha_1 \alpha_2 k^4 U^4 \{ -25 \gamma^2 v^2 [Q(2-5\alpha_1 \alpha_2) \\
& - 2k^2 (1-2\alpha_1 \alpha_2)] + 11 [v^4 + \gamma^2 v^2 [Q(\alpha_1 \alpha_2 + 2) + 4k^2 (\alpha_1 \alpha_2 \\
& \cdot (\alpha_2 - \alpha_1 - 12\alpha_1 \alpha_2 + 7) - 1)] + 2\gamma k^3 B (2\alpha_1 \alpha_2 \gamma^{2Q+v^2(1-\alpha_1 \alpha_2)}) \\
& + \gamma^4 Q(\alpha_1 \alpha_2 Q + 2\alpha_1 \alpha_2 k^2 (3\alpha_1 - \alpha_2))] \} + 2k^2 U^2 \{ \alpha_1 \alpha_2 \{ v^4 [\gamma B k^3 \\
& \cdot (2Q-3k^2) - 2v^2 k^2 - k(\alpha_2 - \alpha_1)] + \gamma^4 k Q \{ 4v^2 k [k^2 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) \cdot \\
& + Q((\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - \alpha_1 \alpha_2)] - 2\alpha_1 \alpha_2 Q(\alpha_2 - \alpha_1) \} \\
& + \gamma^2 v^2 \{ k(\alpha_2 - \alpha_1)(3Q\alpha_1 \alpha_2 + 2(k^2 - 2Q)) + 2\gamma k^3 B Q(Q \\
& - k^2 (2\alpha_1 \alpha_2 + 1)) + v^2 [Q^2 + 4k^4 \alpha_1 (1-2\alpha_2) - k^2 Q(2(\alpha_1 \alpha_2 + \alpha_2 - \alpha_1) \\
& + 5)] \} \} - v^2 \{ k^2 v^4 (2\alpha_1 \alpha_2 - 1) - \gamma v^2 k^5 B (2-5\alpha_1 \alpha_2) \\
& + \gamma^2 \{ \alpha_1^2 \alpha_2^2 k Q (\alpha_2 - \alpha_1) + v^2 k^2 [Q(5\alpha_1 \alpha_2 - 2\alpha_1^2 \alpha_2^2 - 2) \\
& + 2k^2 [(\alpha_2 - \alpha_1)(1-5\alpha_1 \alpha_2) + \alpha_1 \alpha_2 (2\alpha_1 \alpha_2 - 7) + 1]] \} \} \\
& + 2\alpha_1 \alpha_2 k^3 v^4 (\gamma^2 Q(1-2\alpha_1 \alpha_2) + \alpha_2 v^2) + v^4 \{ \gamma^2 k [k^2 Q(4\alpha_1 \alpha_2 \\
& \cdot (3\alpha_2 + \alpha_1 - \alpha_1 \alpha_2) - 2) - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1)(Q^2 + 2k^4)] +
\end{aligned}$$

$$\begin{aligned}
& + v^2 \{ v^2 k^4 + k^2 (2\alpha_1 \alpha_2 (2\alpha_2 + \alpha_1) - 1) - \gamma k^5 B [Q - 2k^2 + 2\alpha_1 \alpha_2 \\
& \cdot (3k^2 - 2Q)] + 2 \gamma^2 k^2 \alpha_1 [2k^2 Q (2\alpha_1 (2\alpha_2 - \alpha_1) - 1) \\
& + 4\alpha_1 \alpha_2 k^2 + \alpha_2 Q (1 - Q) - 4k^4 (1 + 4\alpha_2^2)] \} \}
\end{aligned}$$

$$\begin{aligned}
A_2 = & 1Uk \{ 4\alpha_1^2 \alpha_2^2 \gamma^2 k^6 U^6 (\alpha_2 - \alpha_1) + \alpha_1 \alpha_2 k^4 U^4 \{ \gamma^2 v^2 (\alpha_2 - \alpha_1) \\
& \cdot [2k^2 - Q (2 - \alpha_1 \alpha_2)] + 15 [\gamma^2 v^2 k^2 [2(\alpha_2 - \alpha_1) (3\alpha_1 \alpha_2 - 2) \\
& + 2(2 - 9\alpha_1 \alpha_2)] + 2 \gamma^2 v^2 Q [\alpha_1^2 \alpha_2 - 1] + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \\
& - Q(\alpha_2 - \alpha_1)] - 2\alpha_1 \alpha_2 \gamma^2 k - v^4 (\alpha_2 - \alpha_1) - 2k^3 B \gamma (2\alpha_1^2 \alpha_2 \gamma^2 Q + v^2) \} \\
& + 2k^2 U^2 \{ 2\alpha_1 \alpha_2 \{ 2k^2 v^6 (\alpha_2 - \alpha_1) + v^4 \{ \gamma^2 [(\alpha_2 - \alpha_1) (3k^2 (Q - k^2) \\
& - Q^2) + 2k^2 (4\alpha_1 \alpha_2 - 1) (2(Q + k^2 (k^2 - 1)) + k^2 Q)] - k \\
& - \gamma k^5 B (\alpha_2 - \alpha_1) \} + \gamma^2 v^2 k [2k (2\alpha_1 \alpha_2 - 1) - 3\alpha_1 \alpha_2 Q \\
& - \gamma k^2 Q B (Q - k^2) (\alpha_2 - \alpha_1)] \} + v^2 \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k (3Q - 4k^2) \\
& + v^2 (\alpha_2 - \alpha_1) [v^2 k^2 (2\alpha_1 \alpha_2 - 1) + \gamma k^5 B (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 \\
& \cdot [Q (5\alpha_1 \alpha_2 - 2) + 4k^2 (1 + 2\alpha_1 \alpha_2 (1 - 2\alpha_1 \alpha_2)) + 2(Q + 2\alpha_1^2 \alpha_2)] \} \} \\
& + 3 [2\alpha_1 \alpha_2 v^4 k^3 (\gamma^2 (\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) + \alpha_1 v^2)] - v^4 \{ v^4 k^4 (\alpha_2 - \alpha_1) \\
& - k^3 v^2 [(\alpha_2 - \alpha_1) (1 - \alpha_1 \alpha_2) - \alpha_1 \alpha_2 + \gamma k^2 B (\alpha_2 - \alpha_1) (Q - 2k^2)] \\
& + \gamma^2 \{ k [\alpha_1 \alpha_2 (Q - k^2) (Q - 2k^2) - k^2 Q (1 - 2\alpha_1 \alpha_2) (2(\alpha_2 - \alpha_1) + \alpha_1 \alpha_2)] \\
& + 2v^2 k^2 [(\alpha_2 - \alpha_1) [(2k^2 + Q) (k^2 - \alpha_1 \alpha_2 (2k^2 + Q)) - 2\alpha_1 \alpha_2 k^4] +
\end{aligned}$$

$$\begin{aligned}
& + k^2 [2(1-4\alpha_1\alpha_2 + \alpha_1\alpha_2(5k^2-4)) + Q(1-3\alpha_1\alpha_2)] \} \} \} \\
& - 2k^6 U^6 \alpha_1\alpha_2 \gamma \{ 11[2\alpha_1\alpha_2 \gamma^2 Q + v^2(2-5\alpha_1\alpha_2)] - 2\alpha_1\alpha_2 [2 \gamma^2 \\
& \cdot (Q+4\alpha_1 k^2) + 2k^3 B \gamma + 3v^2] \} + k^4 U^4 \{ 5k^2 \gamma v^4(2-7\alpha_1\alpha_2 + 2\alpha_1^2\alpha_2^2) \\
& - \alpha_1\alpha_2 \gamma \{ v^2 \{ \alpha_1\alpha_2 k(\alpha_2-\alpha_1) + v^2(4-3k^2) + 2\gamma k^3 B(Q(1-\alpha_1\alpha_2) \\
& - k^2) + \gamma^2 \{ Q^2(2-5\alpha_1\alpha_2) + 2Qk^2[2(\alpha_2-\alpha_1)(\alpha_1\alpha_2-1) - 6\alpha_1\alpha_2+1] \\
& - 8k^4\alpha_1 \} \} - 2\alpha_1\alpha_2 \gamma^2 kQ(\alpha_2-\alpha_1) \} + 15\alpha_1\alpha_2 \{ k^3 B v^4 \\
& + \gamma^3 Q[v^2(3\alpha_1\alpha_2 Q - 4k^2(\alpha_2-\alpha_1)(1-2\alpha_1\alpha_2) - 2\alpha_1\alpha_2 k(\alpha_2-\alpha_1) \\
& + 2\alpha_1\alpha_2 \gamma Qk^2(kB-2\gamma) + \gamma v^2[k(\alpha_2-\alpha_1)(\alpha_1\alpha_2-2) + v^2 \\
& + (2k^2\alpha_1(2-3\alpha_1) + Q) + 2\gamma k^3 BQ(1-\alpha_1\alpha_2)] \} \} + k^2 U^2 \\
& \cdot 12\alpha_1\alpha_2 \gamma v^4 k^3(\alpha_2-\alpha_1) + 2\alpha_1\alpha_2 \gamma v^2 \{ v^2 k[(Q-k^2)((\alpha_2-\alpha_1) \\
& + \gamma k^3 B(Q-2k^2)) - v^2 k(2Q-3k^2)] + \gamma^2 \{ kQ(Q-k^2)(\alpha_2-\alpha_1)(2-3\alpha_1\alpha_2) \\
& + 2v^2 k^2 [Q^2(2\alpha_1\alpha_2 - \alpha_2 + \alpha_1) + 2k^4(4\alpha_1\alpha_2 - \alpha_2 + \alpha_1) + 3k^2 Q(\alpha_2 - \alpha_1) \\
& + 2(4\alpha_1\alpha_2 - 1)(Q-k^2)] \} \} + k^3 v^6 \{ \gamma(\alpha_2-\alpha_1)[(Q-2k^2) \\
& \cdot (1-\alpha_1\alpha_2) + \alpha_1\alpha_2(Q-k^2)] + k^4 B v^2 + 2\gamma v^2 k[2\alpha_1\alpha_2(2k^2+Q) \\
& + (\alpha_2-\alpha_1)(k^2+Q)] + \alpha_1\alpha_2 \gamma [(Q-k^2)(\alpha_2-\alpha_1) - (Q-2k^2)] \} \\
A_1 = & 1kU \{ 8\alpha_1\alpha_2 \gamma k^6 U^6(\alpha_2-\alpha_1)[2\alpha_1\alpha_2 \gamma^2 Q + v^2(2-\alpha_1\alpha_2)] + k^4 U^4 \\
& \cdot \{ -4k^2 \gamma v^4(2-3\alpha_1\alpha_2) + 2\alpha_1\alpha_2 \gamma \{ v^4(\alpha_2-\alpha_1)(3k^2-Q) -
\end{aligned}$$

$$\begin{aligned}
& - 2\alpha_1\alpha_2 \gamma^2 k Q + v^2 \left\{ \gamma^2 [Q^2(\alpha_2 - \alpha_1)(\alpha_1\alpha_2 - 2) + 2k^2 Q(\alpha_2 - \alpha_1)] \right. \\
& \cdot (1 - 2\alpha_1\alpha_2) - 4\alpha_1\alpha_2 - 16\alpha_1^2\alpha_2 k^4 - 5\alpha_1\alpha_2 k - 2 \gamma k^3 B(\alpha_2 - \alpha_1) \\
& \cdot (Q - k^2) \left. \right\} - 4k^2 U^2 \left\{ 2\alpha_1\alpha_2 \gamma v^4 k^3 (1 - \alpha_1\alpha_2) + v^2 \left\{ k^5 B v^4 \right. \right. \\
& \cdot (1 - 2\alpha_1\alpha_2) + \gamma^3 \alpha_1^2 \alpha_2^2 k Q (3Q - 4k^2) + \gamma v^2 k [k^2 (2 - 9\alpha_1\alpha_2 + 4\alpha_1^2 \alpha_2^2) \\
& + \alpha_1\alpha_2 Q] + \gamma^2 v^2 k^5 B [2Q(1 - 3\alpha_1\alpha_2) - \alpha_1\alpha_2(\alpha_2 - \alpha_1)] \\
& + \gamma k^2 v^4 \left\{ k^2 [(\alpha_2 - \alpha_1)(7\alpha_1\alpha_2 - 2) + 4\alpha_1\alpha_2(1 - 4\alpha_1\alpha_2) - 2] \right. \\
& + (\alpha_2 - \alpha_1) [4k^4(3\alpha_1\alpha_2 - 1) - 4\alpha_1\alpha_2 + Q] \left. \right\} - 2\alpha_1\alpha_2 \gamma^3 v^2 k^2 Q \\
& \cdot [k^2(2(\alpha_2 - \alpha_1) - 12\alpha_1\alpha_2 + 11) + Q(\alpha_2 - \alpha_1)] \left. \right\} + 2[\alpha_1\alpha_2 \gamma v^6 k^3 \\
& \cdot (Q - k^2) + \alpha_1\alpha_2(\alpha_2 - \alpha_1) \gamma v^6 k^3 (Q - 2k^2)] + \alpha_1^2 \alpha_2^2 \gamma^2 k^8 U^8 \\
& + \alpha_1\alpha_2 k^6 U^6 \left\{ 3 \gamma^2 v^2 [Q(2 - 5\alpha_1\alpha_2) - 2k^2(1 - 2\alpha_1\alpha_2)] \right. \\
& - 7 \left\{ v^4 + \gamma^2 v^2 [Q(\alpha_1\alpha_2 + 2) + 4k^2(\alpha_1\alpha_2(\alpha_2 - \alpha_1 + 7 - 12\alpha_1\alpha_2) - 1)] \right. \\
& + 2 \gamma k^3 B(2\alpha_1\alpha_2 \gamma^2 Q + v^2(1 - \alpha_1\alpha_2)) + \gamma^4 Q(\alpha_1\alpha_2 Q + 2\alpha_1\alpha_2 k^2 \\
& \cdot (3\alpha_1 - \alpha_2) \left. \right\} + k^4 U^4 \left\{ 5\alpha_1\alpha_2 \left\{ v^4 [\gamma k^3 B(2Q - 3k^2) - 2v^2 k^2 \right. \right. \\
& - k(\alpha_2 - \alpha_1)] + \gamma^4 k Q \left\{ 4v^2 k [k^2(\alpha_2 - \alpha_1 - 2\alpha_1\alpha_2) + Q(\alpha_2 - \alpha_1) \right. \\
& \cdot (\alpha_1\alpha_2 - 1) - \alpha_1\alpha_2] - 2\alpha_1\alpha_2 Q(\alpha_2 - \alpha_1) \left. \right\} + \gamma^2 v^2 \left\{ k(\alpha_2 - \alpha_1) \right. \\
& \cdot (3Q\alpha_1\alpha_2 + 2(k^2 - 2Q)) + 2 \gamma k^3 B Q(Q - k^2(2\alpha_1\alpha_2 + 1)) \\
& + v^2 [Q^2 + 4k^4 \alpha_1(1 - 2\alpha_2) - k^2 Q(2(\alpha_1\alpha_2 + \alpha_2 - \alpha_1) + 5)] \left. \right\} \left. \right\} -
\end{aligned}$$

$$\begin{aligned}
& - 3V^2 \{ k^2 V^4 (2\alpha_1 \alpha_2 - 1) - \gamma V^2 k^5 B (2 - 5\alpha_1 \alpha_2) + \gamma^2 \{ \alpha_1^2 \alpha_2^2 k Q \\
& \cdot (\alpha_2 - \alpha_1) + V^2 k^2 [Q(5\alpha_1 \alpha_2 - 2\alpha_1^2 \alpha_2^2 - 2) + 2k^2 ((\alpha_2 - \alpha_1)(1 - 5\alpha_1 \alpha_2) \\
& + \alpha_1 \alpha_2 (2\alpha_1 \alpha_2 - 7) + 1)] \} \} + k^2 U^2 \{ -6\alpha_1 \alpha_2 k^3 V^4 (\gamma^2 Q (1 - 2\alpha_1 \alpha_2) \\
& + \alpha_2 V^2) + V^4 \{ \gamma^2 k [k^2 Q (4\alpha_1 \alpha_2 (3\alpha_2 + \alpha_1 - \alpha_1 \alpha_2) - 2) \\
& - \alpha_1 \alpha_2 (\alpha_2 - \alpha_1) (Q^2 + 2k^4)] + V^2 \{ k^4 V^4 + k^3 (2\alpha_1 \alpha_2 (2\alpha_2 + \alpha_1) - 1) \\
& - \gamma k^5 B [Q - 2k^2 + 2\alpha_1 \alpha_2 (3k^2 - 2Q)] + 2\gamma^2 k^2 \alpha_1 [2k^2 Q (2\alpha_1 (2\alpha_2 - \alpha_1) \\
& - 1) + 4\alpha_1 \alpha_2 k^2 + \alpha_2 Q (1 - Q) - 4k^4 (1 + 4\alpha_2^2)] \} \} \} - k^5 V^8 (\alpha_2 - \alpha_1 - 2\alpha_1 \alpha_2) \\
& = 1kU \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k^8 U^8 (\alpha_2 - \alpha_1) - \alpha_1 \alpha_2 k^6 U^6 \{ \gamma^2 V^2 (\alpha_2 - \alpha_1) \\
& \cdot [Q(2 - \alpha_1 \alpha_2) - 2k^2] + \gamma^2 V^2 \{ k^2 [2(\alpha_2 - \alpha_1) (3\alpha_1 \alpha_2 - 2) \\
& + 2(2 - 9\alpha_1 \alpha_2)] + 2Q(\alpha_1^2 \alpha_2 - 1) \} + 2\alpha_1 \alpha_2 \gamma^4 Q [2k^2 (2\alpha_1 - \alpha_2) \\
& - Q(\alpha_2 - \alpha_1)] - 2\alpha_1 \alpha_2 \gamma^2 k - V^4 (\alpha_2 - \alpha_1) - 2k^3 B \gamma [2\alpha_1^2 \alpha_2 \gamma^2 Q + V^2] \} \\
& - k^4 U^4 \{ \alpha_1 \alpha_2 \{ 2k^2 V^6 (\alpha_2 - \alpha_1) + V^4 \{ \gamma^2 [(\alpha_2 - \alpha_1) (3k^2 (Q - k^2) - Q^2) \\
& + 2k^2 (4\alpha_1 \alpha_2 - 1) (2(Q + k^2 (k^2 - 1)) + k^2 Q)] - k - \gamma k^5 B (\alpha_2 - \alpha_1) \} \\
& + \gamma^2 V^2 k [2k (2\alpha_1 \alpha_2 - 1) - 3\alpha_1 \alpha_2 Q - \gamma k^3 B Q (Q - k^2) (\alpha_2 - \alpha_1)] \} + V^2 \\
& \cdot \{ -\alpha_1^2 \alpha_2^2 \gamma^2 k (3Q - 4k^2) + V^2 (\alpha_2 - \alpha_1) [V^2 k^2 (2\alpha_1 \alpha_2 - 1) + \gamma k^5 B \\
& \cdot (2 - \alpha_1 \alpha_2) + \gamma^2 k^2 [Q(5\alpha_1 \alpha_2 - 2) + 4k^2 (1 + 2\alpha_1 \alpha_2 (1 - 2\alpha_1 \alpha_2)) \\
& + 2(Q + 2\alpha_1^2 \alpha_2)] \} \} + k^2 U^2 \{ 2\alpha_1 \alpha_2 V^4 k^3 [\gamma^2 (\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) +
\end{aligned}$$

$$\begin{aligned}
& + \alpha_1 v^2)] - v^4 \{ k^4 v^4 (\alpha_2 - \alpha_1) - k^3 v^2 [(\alpha_2 - \alpha_1)(1 - \alpha_1 \alpha_2) - \alpha_1 \alpha_2 \\
& + \gamma k^2 B(Q - 2k^2)(\alpha_2 - \alpha_1)] + \gamma^2 \{ k [\alpha_1 \alpha_2 (Q - k^2)(Q - 2k^2) \\
& - k^2 Q(1 - 2\alpha_1 \alpha_2)(2(\alpha_2 - \alpha_1) + \alpha_1 \alpha_2)] + 2v^2 k^2 [(\alpha_2 - \alpha_1) \\
& \cdot [(2k^2 + Q)(k^2 - \alpha_1 \alpha_2(2k^2 + Q)) - 2\alpha_1 \alpha_2 k^4] + k^2 [2(1 - 4\alpha_1 \alpha_2 \\
& + \alpha_1 \alpha_2(5k^2 - 4)) + Q(1 - 3\alpha_1 \alpha_2)] \} \} \} - k^5 v^8 (1 - 2\alpha_1 \alpha_2) \} \\
& - \alpha_1 \alpha_2 \gamma k^8 U^8 \{ 2\alpha_1 \alpha_2 \gamma^2 Q + v^2(2 - 5\alpha_1 \alpha_2) + \alpha_1 \alpha_2 [2\gamma^2(Q + 4\alpha_1 k^2) \\
& + 2k^3 B\gamma + 3v^2] \} + k^6 U^6 \{ - \gamma k^2 v^4(2 - 7\alpha_1 \alpha_2 + 2\alpha_1^2 \alpha_2^2) - \alpha_1 \alpha_2 \gamma \\
& \cdot \{ v^2 \{ \alpha_1 \alpha_2 k(\alpha_2 - \alpha_1) + v^2(Q - 3k^2) + 2\gamma k^3 B(Q(1 - \alpha_1 \alpha_2) - k^2) \\
& + \gamma^2 \{ Q^2(2 - 5\alpha_1 \alpha_2) + 2Qk^2 [2(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - 5\alpha_1 \alpha_2 - 1] \\
& - 8k^4 \alpha_1 \} \} - 2\alpha_1 \alpha_2 \gamma^2 k Q(\alpha_2 - \alpha_1) \} + \alpha_1 \alpha_2 \{ k^3 B v^4 \\
& + \gamma^3 Q [v^2(3\alpha_1 \alpha_2 Q - 4k^2(\alpha_2 - \alpha_1)(1 - 2\alpha_1 \alpha_2)) - 2\alpha_1 \alpha_2 k(\alpha_2 - \alpha_1) \\
& + 2\alpha_1 \alpha_2 \gamma Q k^2(Bk - 2\gamma)] + \gamma v^2 [k(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 2) + v^2(2k^2 \alpha_1 \\
& \cdot (2 - 3\alpha_1) + Q) + 2\gamma k^3 B Q(1 - \alpha_1 \alpha_2)] \} \} + k^4 U^4 \{ v^6 k^5 B(\alpha_2 - \alpha_1 \\
& - 2\alpha_1 \alpha_2) + \gamma v^2 \{ k^3 B \gamma v^2 [2k^2 Q((\alpha_2 - \alpha_1)(1 - \alpha_1 \alpha_2) - 2\alpha_1 \alpha_2) \\
& + \alpha_1 \alpha_2(Q^2 + 2k^4)] + k v^2(\alpha_2 - \alpha_1) [2k^2(1 - 2\alpha_1 \alpha_2) + \alpha_1 \alpha_2(\alpha_2 - \alpha_1) \\
& \cdot (Q - 1)] + \alpha_1 \alpha_2 k Q \gamma^2(\alpha_2 - \alpha_1) [2Q(1 - \alpha_1 \alpha_2) + k^2(3\alpha_1 \alpha_2 - 2)] \\
& + v^4 \{ k^2 Q [(\alpha_2 - \alpha_1)(\alpha_1 \alpha_2 - 1) - 5\alpha_1 \alpha_2] + 2k^4 [(\alpha_2 - \alpha_1)(1 - 5\alpha_1 \alpha_2) - 3] +
\end{aligned}$$

$$\begin{aligned}
& + \alpha_1 \alpha_2 (2k^2 + 1) \} + 2k^2 \gamma^2 v^2 \{ \alpha_1 \alpha_2 Q [4\alpha_1 \alpha_2 - 1 + Q(1 - 3(\alpha_2 - \alpha_1) \\
& - 6\alpha_1 \alpha_2)] + k^2 [2\alpha_1 \alpha_2 (k^2 (4\alpha_1 \alpha_2 - \alpha_2 + \alpha_1) - 2\alpha_1 \alpha_2] \\
& + Q(1 - 2\alpha_1 \alpha_2 (3 - 4\alpha_1 \alpha_2)) + (\alpha_2 - \alpha_1)(4\alpha_1 \alpha_2 - 1)) \} \} \\
& + k^2 v^2 \{ v^6 k^3 \{ \gamma (\alpha_2 - \alpha_1) [(Q - 2k^2)(1 - \alpha_1 \alpha_2) + \alpha_1 \alpha_2 (Q - k^2)] \\
& + k^4 B V^2 + 2 \gamma k V^2 [2\alpha_1 \alpha_2 (2k^2 + Q) + (\alpha_2 - \alpha_1)(k^2 + Q)] \\
& - \alpha_1 \alpha_2 \gamma [(Q - k^2)(\alpha_2 - \alpha_1) - (Q - 2k^2)] \} \}
\end{aligned}$$

Area-time tradeoffs for parallel merging

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Abstract

In this paper, the VLSI complexity for the problem of merging two sorted arrays is studied. Let A and T be the chip area and computation time of a VLSI circuit that merges two sorted arrays of length N , by deriving the information transfer between the two sides of a partition of the chip, it is shown that $AT^2 = \Omega(N^2 \log^2 N)$. This result indicates that the inherent computational complexities for sorting and merging are asymptotically identical in the VLSI mode, unlike in the conventional model of sequential computation.

(**Keywords** : VLSI algorithms/parallel merging/area-time tradeoffs/computational complexities)

Introduction

With the advent of Very Large Scale Integration (VLSI), the chip area and computation time have been reduced dramatically. As a result, new methodologies and techniques are employed to design and manufacture small and expensive chips. Since in VLSI the wires, as opposed to the processing elements, dominate the manufacturing cost and computation time, the chip area rather than the number of logical elements is counted as the main measure of the complexity of the computation. Details on VLSI technology are discussed in Mead and Conway¹.

One important and interesting area in VLSI research is to obtain lower bounds for the area-time tradeoffs for certain problems. During the past few years, various models for VLSI computation were developed¹⁻⁵. Based on these models lower bounds for area - time tradeoffs are obtained for problems such as discrete Fourier transform⁴, integer multiplication^{2,6} and matrix multiplication and some related problems⁷, sorting⁸ transitive function⁵ and a number of predicates^{3,8,9,10}.

In this paper, the problem of merging two sorted arrays is considered. Following the VLSI models discussed in literature^{1,2,4,11}. We derive the lower bound for the area-time tradeoffs for this problem. Let A and T denote the chip area and computation time required to merge two sorted arrays of length N , we will show that $AT^2 = \Omega(N^2 \log^2 N)$ and $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$, for $0 \leq x \leq 1$.

The Merging Problem and VLSI Model

Let $D = \{0, 1, \dots, K-1\}$ be a set of K elements. Each element in D is called a word and can be represented with $\lceil \log K \rceil$ bits. Let $D_N = \{(x_1, x_2, \dots, x_N) \mid x_1 \leq \dots \leq x_N, x_i \in D\}$ be the set containing all the sorted arrays of length N . Let $\|A\|$ denote the number of elements contained in a set A , then it is well known combinatorial result that

$$\|D_N\| = \binom{K+N-1}{N} \quad (1)$$

The merging problem can be characterized by the function $F : D_N \times D_N \rightarrow D_{2N}$, such that $F(x_1, \dots, x_N, y_1, \dots, y_N) = (z_1, \dots, z_{2N})$, where $X = (x_1, \dots, x_N)$, $Y = (y_1, \dots, y_N)$, D_N , $Z = (z_1, \dots, z_{2N}) \in D_{2N}$, and $\{x_1, \dots, x_N\} \cup \{y_1, \dots, y_N\} = \{z_1, \dots, z_{2N}\}$. Arrays X and Y are the two input arrays to be merged, and array Z is the sorted array resulting from the merge.

The VLSI model used in this paper is adopted from those proposed in literature^{1,2,4}. A VLSI circuit in our model can be viewed as the layout of a graph in which nodes correspond to logical gates and edges correspond to wires. While the nodes serve as either processing elements or I/O ports, the wires are used for interconnection between gates. We assume that chip layout of a VLSI circuit is a convex planar region. A wire in layout has minimal width $\lambda > 0$ and can transmit 1 bit of information. It is assumed that at most $v \geq 2$ wires can overlap at any point in the layout of a VLSI circuit, i.e., there are at most v layers in a chip. Each node can store a bit and occupies at least $\rho \geq \lambda^2$ area. As for the processing time, it is assumed that a minimal delay τ is required to transmit one bit through a node; this includes the delay over the wires. We also assume that each input is read exactly once and read in form a distinct input port, and that the times and locations at which the inputs are supplied and output are delivered are fixed and independent of the input values. The above assumptions reflect the state of nMOS circuit design methodology and fabrication technology¹. Details on these assumptions can be found in literature^{1,2,11}.

Lower Bounds

Based on the VLSI model described in the previous section, we will derive in this section a lower bound for AT^2 , where A and T are the chip area and computation time of a VLSI circuit that merges two sorted arrays.

Our approach is now a classical one and consists of partitioning the circuit into two regions with roughly equal sizes, and then derive the minimal amount of information necessary to flow between the two sides of the partition during the course of computation. This technique was originally developed in literature⁴ and was used to obtain the area time complexity of various problems in literature^{2,4-8}. Consider a function $F(x_1, \dots, x_N) = (z_1, \dots, z_m)$ and a VLSI circuit implementing F . Let L and R be the two regions obtained by partitioning the circuit with a chord perpendicular to the diameter of the layout. We will denote this partition by (L, R) . Since it is always possible to slide the chord appropriately such that the number of input variables in R is equal to $s = \lfloor N/2 \rfloor$, we will assume throughout this paper that this is true for any partition (L, R) . Also, for the sake of clarity in the remainder of this section, we assume that each input variable has all its bits input on the same side of partition. To be general we would have to define that a variable is input on the side of the partition where the majority of its bits are input. Since we would still consider at least half of the total number of bits, this would only change our result by a factor of 2.

Let $X_R = (x_{i1}, \dots, x_{is})$ $i_1 \leq \dots \leq i_s$, be the variables of X in R and $Z_R = (z_{j1}, \dots, z_{jr})$, be the variables of Z in R , then the information flow from L to R is defined in the following definition.

Definition 1 : Let

$$F_{X_R \rightarrow C}^{Z_R} = (Z_{j1}, \dots, Z_{jr})|_{x_{i1} = c_1, \dots, x_{is} = c_s},$$

where $C(c_1, \dots, c_s) \in D_s$ be the restriction of F to Z_R obtained by setting the input variables x_{i1}, \dots, x_{is} to the constants c_1, \dots, c_s respectively. The information -flow from L to R is defined by :

$$I(F) = \phi_{L \rightarrow R} + \phi_{R \rightarrow L}.$$

Definition 2 : The cross-flow $I(F)$ that measures the amount of information that must flow between L and R during the computation of F is defined by

$$\phi_{L \rightarrow R} = \left\lceil \log \max_{C \in D_s} \left\| F \begin{matrix} Z_R \\ X_R \end{matrix} = C \right\| \right\rceil \quad (2)$$

The information-flow from R to L , $\phi_{R \rightarrow L}$ is defined similarly.

The cross flow $I(F)$ is related to AT^2 by the following lemma originally due to Thompson⁴.

Lemma 1 : The are A and the computation time T of a VLSI layout satisfy :

$$AT^2 \geq \frac{1}{2} \left(\frac{\lambda \tau}{v} \right)^2 I^2(F), \quad (3)$$

where λ , τ and v are the parameters discussed in the previous section.

Lets consider now the problem of merging two sorted arrays. Let $F(x_1, \dots, x_N, y_1, \dots,$

$y_N) = (z_1, \dots, z_{2N})$ be the function that implements merging. For $1 \leq m \leq N-1$ by choosing $y_1 = y_2 = \dots = y_m = 0$ and $y_{m+1} = \dots = y_N = K-1$, the restriction of F ,

$$F_m := F: (x_1, \dots, x_N, 0, \dots, 0, K-1, \dots, K-1) \rightarrow (0, \dots, 0, x_1, \dots, x_N, K-1, \dots, K-1), \quad (4)$$

is the function that shifts each input x_j by m position. Note that there are m 0's and $N-m(K-1)$'s in both parenthesis. Moreover, the sub function $id: (x_1, \dots, x_N) \rightarrow (z_{m+1}, \dots, z_{m+N})$ is the identify function in that $z_{m+1} = x_j$. The function F_0 and F_N are defined similarly by setting all the y_j 's to $(K-1)$ and 0 respectively. The cross flow of id is derived in lemma 2. The following notation is useful in our derivations: Given a set of subscripted variables $U = \{u_{i_1}, \dots, u_{i_p}\}$ we let $S(U)$ denote the set of subscripts $\{i_1, \dots, i_p\}$.

Lemma 2 : Let (L, R) be a portion of the circuit that implements the identify function $id(x_1, \dots, x_N) = (z_1, \dots, z_N)$, where $X = (x_1, \dots, x_N)$, $Z = (z_1, \dots, z_N) \in D_{Ns}$ and $z_i = x_j$; for $i \leq j \leq N$. Let X_L and X_R ($X_L \cup X_R = X$) denote the sets of variables of X that are in L and R respectively. Similarly, let Z_L and Z_R and $(Z_L \cup Z_R = Z)$ denote the sets of variables of Z that are in L and R respectively. Let $\|S(X_L) \cap S(Z_R)\| + \|S(X_R) \cap S(Z_L)\|$, the cross-flow of id satisfies.

$$I(id) = \Omega(k \log k), \quad (5)$$

If $K = N^{1+\varepsilon}$ for some fixed value $\varepsilon > 0$.

Proof : Assume $S(X_L) \cap S(X_R) = \{i_1, \dots, i_p\}$ where $i_1 \leq \dots \leq i_p$. By grouping all the variables with consecutive indices together, the set $\{x_{i_1}, \dots, x_{i_p}\}$ can be partitioned into t disjoint sets :

$$\{x_{i_1}, \dots, x_{i_p}\} = \{x_{i_1}, \dots, x_{i_{p_1}}\} \cup \{x_{i_{p_1+1}}, \dots, x_{i_{p_1+p_2}}\} \cup \dots \cup \{x_{i_{p_1+\dots+p_{t-1}+1}}, \dots, x_{i_{p_1+\dots+p_t}}\},$$

where p_j is the number of the variables in the j^{th} group. Note that $p_1 + \dots + p_t = p$ and $i_{p_1} = i_1 + p_1 - 1$, $i_{p_1+p_2} = i_{p_1+1} + p_2 - 1$, ..., etc.

Now lets consider $\phi_{L \rightarrow R}$. By choosing proper constant values for the input variables whose indices are not in $\{i_1, \dots, i_p\}$, we can derive the lower bound for $\phi_{L \rightarrow R}$ by counting the number of joints in the range of

$$\left(z_{i_1}, \dots, z_{i_p} \right) \Big| x_j = c_j, j \notin \{i_1, \dots, i_p\},$$

since by the definition of $\phi_{L \rightarrow R}$,

$$\phi_{L \rightarrow R} \geq \log \left\| \left(z_{i_1}, \dots, z_{i_p} \right) \Big| x_j = c_j, j \notin \{i_1, \dots, i_p\} \right\|$$

The constant value c_j assigned to $x_j, j \notin \{i_1, \dots, i_p\}$ is defined as follows :

- (i) $c_j = 0$, if $j \leq i_1$,
- (ii) $c_j = a_n$, if $j \leq i_1$, if $i_{p_1+\dots+p_n} < j < i_{p_1+\dots+p_{n+1}}$, for $1 \leq n \leq t-1$,
- (iii) $c_j = a_t$, if $j > i_{p_1+\dots+p_t}$,

where

$$a_n = \sum_{1 \leq i \leq n} (K_i - 1) \text{ and } K_i = \lceil (K-1) p_i/p \rceil \geq 1.$$

Note that the choice of the sequence $\{a_n\}$ is legal, since $\{a_n\}$ is increasing and

$$a_t \sum_{1 \leq i \leq t} (K_i - 1) \leq \sum_{1 \leq i \leq t} (K-1) \frac{p_i}{p} = K-1.$$

with $x_j, j \notin \{i_1, \dots, i_p\}$ being fixed to constant values as above, the cardinality of the range of $(z_1, \dots, z_p) \mid x_j = c_j, j \notin \{i_1, \dots, i_p\}$ is equal to the number of solution to the following inequality :

$$0 \leq x_{i_1} \leq \dots \leq x_{i_{p_1}} \leq a_1 \leq x_{i_{p_1+1}} \leq \dots \leq x_{i_{p_1+p_2}} \leq a_2 \leq \dots \leq a_{t-1} \leq x_{i_{p_1+\dots+p_{t-1}+1}} \leq \dots \leq x_{i_{p_1+\dots+p_t}} \leq a_t, \quad (6)$$

And the log of the number of solutions is a lower bound for $\phi_{L \rightarrow R}$.

From the fact that the inequality

$$0 \leq x_1 \leq \dots \leq x_p \leq K-1 \text{ has } \binom{k+p-1}{p}$$

solution, the total number of solutions to (9) is

$$\binom{K_1 + p_1 - 1}{p_1} \binom{K_2 + p_2 - 1}{p_2} \dots \binom{K_t + p_t - 1}{p_t}$$

thus we have

$$\phi_{L \rightarrow R} \geq \log \prod_{1 \leq j \leq t} \binom{K_j + p_j - 1}{p_j}$$

$$\begin{aligned}
 &= \sum_{1 \leq j \leq t} \log \frac{(K_j + p_j - 1) \dots K_j}{p_j \dots 1} \\
 &\geq \sum_{1 \leq j \leq t} \log \left(\frac{K_j}{p_j} \right)^{p_j} \\
 &\geq \sum_{1 \leq j \leq t} p_j \log \frac{K - 1}{p} \\
 &= p \log \frac{K - 1}{p} \\
 &= \Omega(p \log p).
 \end{aligned}$$

The last equality follows from the fact that $p < N$ and the assumption that $K = N^{1+\varepsilon}$ for some fixed value $\varepsilon > 0$.

Similarly if $\|S(X_R) \cap S(Z_L)\| = q$ ($q = k - p$), then we can show

$$\phi_{R \rightarrow L} = \Omega(q \log q). \quad (7)$$

Since $f(x) = x \log x$ is a convex function, we have

$$\frac{p \log p + q \log q}{2} \geq \frac{p + q}{2} \log \frac{p + q}{2} \quad (8)$$

$$\text{This gives } I(id) = \Omega(k \log k). \quad (9)$$

Consider now the merge problem. Let (L, R) be a partition of the circuit that implements $F(X, Y) = (Z)$ where $X, Y \in D_N$ and $Z \in D_{2N}$. We will introduced some useful notations as follows. Let F_m be the function that shifts each input variable x_i by m positions as defined in (6), and X_L, X_R, Z_L and Z_R be defined the same as in lemma 2. If $\{x_i\}$ $i \in I$ is a set of subscripted variables, then define $X^m = \{X_{i+m}\}$ $i \in I$. Let $\Psi(F_m)$ be defined by

$$\Psi(F_m) = \|S(X_L^m) \cap S(Z_R)\| + \|S(X_R^m) \cap S(Z_L)\|. \quad (10)$$

Note that $\Psi(F_m)$ measures the number of variables that "cross" through the partition of the circuit, i.e. the number of variables whose input ports and output ports lie in different sides of the partition.

The following lemma shows that there exists at least an m , $1 \leq m \leq N$, for which the number of variables crossing the partition is $\Omega(N)$.

Lemma 3 : There exists at least an m , $1 \leq m \leq N$, such that $\Psi(F_m) \geq \lfloor N/8 \rfloor$.

Proof: Let's consider the $\lceil N/2 \rceil$ output variables $x_{\lfloor N/2 \rfloor + 1}, \dots, x_N$ and the $\lceil N/2 \rceil$ output variables $z_{N+1}, \dots, z_{N+\lceil N/2 \rceil}$.

Only for each such z_j and x_i , x_j is mapped to z_j by F_m where $1 \leq m = j-1 \leq N$. Therefore, by counting through all the F_m , $1 \leq m \leq N$, we have

$$\sum_{1 \leq m \leq N} \Psi(F_m) \geq (\lceil N/2 \rceil) \min(l, r), \quad (11)$$

$$\sum_{1 \leq m \leq N} \Psi(F_m) \geq (\lceil N/2 \rceil) \lceil N/2 \rceil / 2 \quad (12)$$

and there must exist an m , $1 \leq m \leq N$, such that $\Psi(F_m) \geq \lfloor N/8 \rfloor$.

where l and r are the number of input variables x_i , $\lfloor N/2 \rfloor + 1 \leq i \leq N$, which are in L and R respectively. Since $\lfloor N/2 \rfloor \leq l$, $r \leq \lceil N/2 \rceil$, we have

$\sum \Psi(F_m) \geq 1 \leq m \leq N \lfloor N/2 \rfloor \lfloor N/2 \rfloor / 2$, and there must exist an m , $1 \leq m \leq N$ such that $\Psi(F_m) \geq \lfloor N/8 \rfloor$

Combining lemma 2 and lemma 3, it follows that

$$I(F_m) = \Omega(N \log N). \quad (13)$$

Theorem : If A is the chip area and T is the computation time required to merge two sorted arrays of lengths N , then

$$AT^2 = \Omega(N^2 \log N) \text{ and} \quad (14)$$

$$AT^{2x} = \Omega(N^{1+x} \log^{2x} N), \quad (15)$$

for $0 \leq x \leq 1$, if $K = N^{1+\varepsilon}$ for a fixed value $\varepsilon > 0$.

Proof: Since F can realize each $F_m, 1 \leq m \leq N$, equation (14) follows directly from lemma 1 and equation (15).

As for equation (15), consider the time when all the $\lceil N/2 \rceil$ input variables $x_{\lceil N/2 \rceil+1}, \dots, x_N$ have been read. None of the $\lceil N/2 \rceil$ variables $z_{N+1}, \dots, z_{N+\lceil N/2 \rceil}$ have been output, since each x_i can be routed to each z_j by some F_m . These $\lceil N/2 \rceil$ output variables can assume $2^{\lceil N/2 \rceil}$ distinct values; the circuit is therefore required to memorize $\lceil N/2 \rceil$ bits of information in order to assume $2^{\lceil N/2 \rceil}$ internal states. From the assumption in section 2 that each node occupies at least ρ area, we conclude that

$$A \geq \rho \lceil N/2 \rceil. \quad (16)$$

Equation (15) then follows directly from equation (14) and (16).

Conclusion

Following the VLSI model described in section 2, we have derived in the previous section lower bounds for the area-time tradeoffs for the merging two sorted arrays of lengths N is $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$, For $0 \leq x \leq 1$, $K = N^{1+\varepsilon}$ for a fixed value $\varepsilon > 0$. This shows that the inherent computational complexities for sorting and merging are asymptotically identical in the VLSI model¹² unlike in the conventional model of sequential computation.

Although we required, in the proof given in the paper, that such input appear on a distinct input port, this assumption can easily be relaxed and it can be assumed that I/O ports are multiplexed. The proof would then follow arguments similar to the ones given in¹² for examples.

Consider the general case of the merging problem in which the lengths of the two arrays to be sorted may not be the same. Lets assume that the lengths of these two arrays be M and N , where $M \geq N$. From our results, it can be shown that the lower bound on area-time complexity for this general problem is $AT^{2x} = \Omega(N^{1+x} \log^{2x} N)$ for $0 \leq x \leq 1$. This lower bound is however not tight for the case when M is very large, compared with N . A typical example of this is the case when $N=1$. In that case, the merging problem is equivalent to the problem of inserting an element into a sorted arrays. An interesting open problem is therefore to obtain better lower bound for this general case of merging problem.

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Equilibrium studies on mixed ligand complexes— Evidence of stacking interactions-solution studies

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Abstract

Interaction of bivalent metals with maltol or kojic acid and selected amino acids (Alanine, β -phenylalanine, L-tyrosine, L-DOPA and tryptophan) has been investigated by potentiometric pH measurements at 30 °C and $\mu = 0.1 \text{ mol dm}^{-3}$ (KNO_3). The stability order of these ternary complexes is in the order Ph alanine < tyrosine < DOPA < Tryptophan. The extra stabilisation and above sequence of order is attributed to stacking interactions in ternary complexes.

(**Keywords:** potentiometry / ternary complexes / formation constants / maltol / kojic acid / amino acids).

In continuation to our earlier work¹⁻³ on ternary metal complexes of γ -pyrones, we now report the formation constants of ternary complexes of type MAL [where M = Co(II), Ni(II), Cu(II) and Zn(II); L = 3-hydroxy-2-methyl-pyran-4-one (maltol) or 5-hydroxy-2(hydroxymethyl)pyran-4-one (kojic acid); A = amino acids (*viz.* alanine, phenyl alanine, tyrosine, tryptophan and 3, 4 dihydroxyphenyl alanine (DOPA))] which have been determined potentiometrically at 30°C and $\mu = 0.1 \text{ mol dm}^{-3}$ (KNO_3) in aqueous medium.

The ligands, maltol and kojic acid are obtained from Lancaster (U.K). The amino acids are obtained from Sigma Chemical Company. The metal salts of Co(II), Ni(II), Cu(II), and Zn(II) are of AnalaR grade and their solutions are standardized volumetrically by titration with the sodium salt of EDTA.⁴ Potentiometric measurements are carried out at 30°C in aqueous medium (with 0.1 M KNO_3 as background electrolyte) using control dynamics pH meter. The pH meter readings are plotted against a (moles of base added per mole of ligand) or m (moles of base added per mole of metal ion). Calculations were carried out with the help of computer program - BEST.⁵ The calculated ternary stability constants are reported in Table 1. Table 2 lists the $\Delta \log K$ values along with $\Delta \Delta \log K$ values. The parameters, $\Delta \log K$ and $\Delta \Delta \log K$ are used to characterize the stability of ternary complexes formed. The extra stability found in ternary complexes is due to stacking interactions.

The stacking interactions, can be quantised with suitable parameters associated with the following equilibrium:

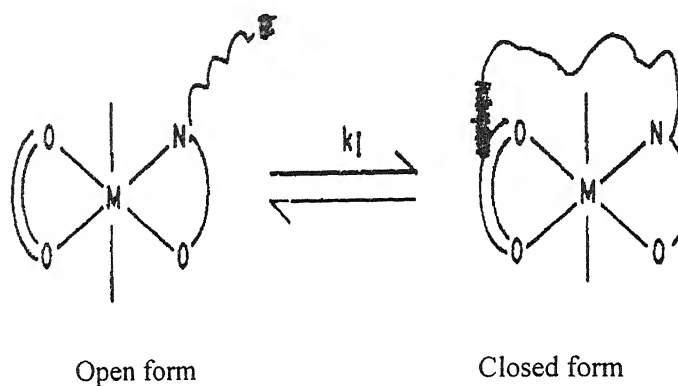


Table 1- Logarithms of stability constants ($\log K_{MLA}^M$) of ternary complexes
 $[T = 30^\circ\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

Secondary Ligands (A)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Kojic acid as primary ligand (L)				
alanine	8.65	10.06	14.05	9.56
Ph.alanine	8.53	9.78	13.78	9.21
Tyrosine	8.02	9.43	13.15	9.08
DOPA	8.65	9.97	14.16	9.23
Tryptophan	8.70	9.99	13.90	9.58
Maltol as primary ligand (L)				
alanine	9.28	10.77	15.14	10.26
Ph.alanine	9.20	10.55	14.91	9.99
Tyrosine	8.70	10.20	14.26	9.83
DOPA	9.34	10.75	15.31	10.01
Tryptophan	9.35	10.71	15.04	10.32

Sigma fit values are in the range ± 0.05 to 0.08 log units

The concentration independent and dimensionless constant K_1 for intramolecular equilibrium is calculated by the relationship:

$$K_1 = 10^{\Delta\Delta\log K - 1} \quad (1)$$

The parameter $\Delta\Delta\log K$ is given by relationship

$$\Delta\Delta\log K = (\Delta\log K_1 - \Delta\log K_2) \quad (2)$$

where $\Delta\log K_2$ is for the reaction $[M^{2+} + L + Ala]$ and $\Delta\log K_1$ relates to the reaction $[M^{2+} + L + \text{other amino acids}]$. The values thus obtained are given in Table 2.

Table 2—Comparison of $\Delta\log K$ and $\Delta\Delta\log K$ values for ternary complexes

$[T = 30^\circ\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

Secondary Ligands (A)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Kojic acid as primary ligand (L)				
alanine	-0.38	-0.37	-0.45	-0.39
Ph alanine	-0.32	-0.27	-0.31	-0.33
	(+0.06)	(+0.10)	(+0.14)	(+0.06)
Tyrosine	-0.29	-0.25	-0.26	-0.26
	(+0.09)	(+0.12)	(+0.19)	(+0.13)
DOPA	-0.26	-0.16	-0.21	-0.26
	(+0.12)	(+0.21)	(+0.24)	(+0.13)

Table 2 Contd

Table 2 Contd

Tryptophan	-0.20 (+0.18)	-0.12 (+0.25)	-0.15 (+0.30)	-0.18 (+0.21)
Maltol as primary ligand (L)				
alanine	-0.35	-0.30	-0.40	-0.32
Ph alanine	-0.25 (+0.10)	-0.14 (+0.16)	-0.22 (+0.18)	-0.18 (+0.14)
Tyrosine	-0.21 (+0.14)	-0.12 (+0.18)	-0.19 (+0.21)	-0.14 (+0.18)
DOPA	-0.17 (+0.18)	-0.02 (+0.28)	-0.10 (+0.30)	-0.11 (+0.21)
Tryptophan	-0.15 (+0.20)	-0.04 (+0.26)	-0.05 (+0.35)	-0.07 (+0.25)

$\Delta \log K = [\log K_{MLA}^M - \log K_{MA}^M + \log K_{ML}^M]$. The $\Delta \log K$ values are presented in paranthesis.

$\Delta \log K = [\Delta \log K_1 - \Delta \log K_2]$, where $\Delta \log K_1$ is for the reaction (M + L + amino acids except alanine) and $\Delta \log K_2$ is for the reaction (M + L + alanine).

Alanine is taken as a reference for zero based stacking interactions

The percentage of stacked isomers in the systems is also calculated with the relationship:

$$\%(MLA)_{st} = [100 * K_1 / (1 + K_1)] \quad (3)$$

The values of K_1 and $\%(MLA)_{st}$ for these systems are presented in Table 3. The perusal of parameters associated with stacking interactions reveal the following observations :

Table 3—Parameter showing the extent of intramolecular stacking interaction in ternary complexes
 $[T = 30^{\circ}\text{C}, \mu = 0.1 \text{ mol dm}^{-3} (\text{KNO}_3), \text{aqueous medium}]$

Secondary Ligands (A)	Parameters	Co(II)	Ni(II)	Cu(II)	Zn(II)
Kojic acid as primary ligand (L)					
Ph alanine	K_1	0.148	0.258	0.380	0.148
	% (MLA)st	12.89	20.50	27.54	12.89
Tyrosine	K_1	0.230	0.3182	0.548	0.348
	% (MLA)st	18.70	24.13	35.44	25.82
DOPA	K_1	0.318	0.622	0.738	0.479
	% (MLA)st	24.13	38.35	42.46	32.38
Tryptophan	K_1	0.513	0.778	0.995	0.622
	% (MLA)st	33.91	43.75	49.88	38.35
Maltol as primary ligand (L)					
Ph alanine	K_1	0.258	0.445	0.513	0.380
	% (MLA)st	20.50	30.79	33.91	27.54
Tyrosine	K_1	0.380	0.513	0.622	0.513
	% (MLA)st	27.54	33.91	38.35	33.91
DOPA	K_1	0.513	0.9054	0.9952	0.622
	% (MLA)st	33.91	47.51	49.88	38.5
Tryptophan	K_1	0.585	0.8197	1.238	0.778
	% (MLA)st	36.91	45.04	55.32	43.75
*Benzimidazole as primary ligand (L)					
Ph alanine	K_1	1.137	1.691	1.344	1.041
	% (MLA)st	53.20	62.83	57.33	51.00
Tyrosine	K_1	1.344	1.818	1.884	1.238
	% (MLA)st	57.33	64.51	65.33	55.31
DOPA	K_1	1.187	1.691	1.454	1.089
	% (MLA)st	54.27	62.83	59.25	52.13
Tryptophan	K_1	1.454	2.235	2.235	1.630
	% (MLA)st	59.25	69.08	69.08	61.97

* Data for benzimidazole is abstracted from the reference. Usha Rani, G & DD Manwal (1998)
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- (a) The stacking interactions decrease in the order: tryptophan > tyrosine > DOPA > ph.alanine. This order can be correlated with the size of the aromatic side chain. Stacking in ternary complexes containing tryptophan results in maximum⁶ stabilization since the surface area of the indole ring is large and permits for efficient stacking with kojic acid or maltol. The phenyl rings of ph.alanine and tyrosine are small and hence lower efficiency of stacking.

The ligand DOPA is an ambidentate ligand. DOPA can bind to metal ion either like glycine using amino carboxylic group or it can bind like pyrocatechol using both oxygens present on phenyl ring. It is well known that in lower pH, DOPA binds to metal ion through amino carboxylate end and at higher pH it binds like catechol. However as observed by Bhattacharya, the present study also shows that DOPA binds in ternary complexes from the amino carboxylate ends over the pH range of 4-7.

- (b) The % of stacking interaction decreases in the order Cu(II) > Ni(II) > Zn(II) > Co(II) with respect to the metal ions. This order is in confirmity with Irving Williams natural order of stabilities⁸.
- (c) The stability sequence with respect to primary ligand is in the order: Maltol > Kojic acid. This sequence is in line with basicity order. Maltol is more basic than kojic acid hence forms more stable complex.
- (d) The present communication deals with stacking interaction between aromatic moiety of one ligand and π electron cloud of another ligand. Earlier we have published a paper in which two ligands have aromatic moieties (eg. benzimidazoles as primary ligand and amino acids as secondary ligand). We thought it worthwhile to compare the extent of stacking interactions in these two different systems. Hence, we have reproduced the data of benzimidazole in Table 3. Comparison of % of stacked form from table 3 reveals the order : [benz-Cu-tryptophan](69.08%) > [maltol-Cu-tryptophan](55.32%) > [kojic acid-Cu-tryptophan] (49.88%). Complex containing benzimidazole forms much better stacked complex than ternary complex of maltol or kojic acid. The reason is simple, the benzimidazole is aromatic whereas maltol or kojic acid are non-aromatic.

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